# FACTORS THAT IMPACT SCALE INHIBITOR MECHANISMS

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## Abstract

The formation of mineral scales such as barium sulphate and calcium carbonate remains an issue for the oil industry, after many years of oil exploration. In the last 10 years, the difficulty in dealing with scale deposition has been accentuated by the appearance of more complex conditions, involving complicated well completions for deepwater or long sub-sea tiebacks. If scale control measures fail in these situations then long distances between the scale deposits and the production platform are present. Intervention into such systems is either impossible or extremely expensive. To combat such problems, the front end engineering design stage (FEED) now attempts to bring together multidisciplinary teams to provide a full risk assessment of all areas in which production chemistry problems might arise. Hence, benefits come from each discipline team having as much knowledge as possible available to them. This thesis aims to fuel this knowledge by developing a fundamental understanding of how various factors, conditions or environmental, impact scale inhibitor mechanisms, so that the results can be incorporated into the FEED process.

Key areas affecting scale inhibitor operation were investigated. From these studies, a number of important findings can be highlighted. The presence of calcium was found to improve scale inhibitor (SI) performance, especially phosphonate types, whilst magnesium ions had little effect on polymeric performances and detrimentally affected the phosphonates' inhibition efficiency (IE). These trends were related to the SI affinity for the divalent ions – polymer PPCA binds to calcium but shows incompatibility at $[Ca^{2+}]$ > 1000ppm - observed as low IE, whilst the phosphonate DETPMP binds with either ion but prefers calcium. Two inhibition mechanisms - nucleation and crystal growth blocking - were identified for different types of SI species and were illustrated using static IE tests relating IE to [SI] left in solution. High IE corresponds to high [SI] and similarly low IE with low [SI]. These initial results have since been investigated further in a additional study. An extensive range of phosphonate and polymeric scale inhibitor species can now be classified as i. either Type 1 or 2 (based on IE, $Ca^{2+}$ and $Mg^{2+}$ sensitivity ration and SI consumption tests) or ii. either Type A or B (based on compatibility/incompatibility with $[Ca^{2+}]$= ~1000-2000ppm+).

A requirement for both homogeneous and heterogeneous nucleation to be investigated for a scaling system was identified, as deposition kinetics can vary requiring different

levels of SI. A [SI] falling below minimum inhibitor concentration (MIC), can promote surface scaling. Hence, scaling systems should be studied experimentally over a range of temperatures, to represent the conditions from sub-sea tiebacks to the production well.

A model was developed from experimental data enabling the prediction of safe sulphate levels and mass of barite deposited. This model can be applied to un-seeded and seeded tests where, as expected, the foreign particles accelerated the reaction to equilibrium with the greatest deposition rate for barite over sand and for a higher surface area over a lower one.

Both theoretical and experimental confirmation of each retention mechanism occurring in a porous medium was achieved. This adsorption/precipitation model has been incorporated into Squeeze VII, an in-house squeeze design software, to allow a better physical description of a squeeze treatment. The predictions of Squeeze VII have also been improved by using the more accurate data for the scale inhibitor return concentrations from core floods due to the better developed analysis techniques.

The direct value of these improvements to industry is significant. These advances reduce OPEX costs and deferred oil production whilst giving the industry the opportunity of improved future lifetime predictions and operations.

## Acknowledgements

Since starting almost 20 years ago as a laboratory research technician, with FAST or the group previously known as the OSRG, I have come into contact with a great number of people who have shown such enthusiasm for their research that it not only rubbed off on me but I was encouraged to accept responsibility and challenge myself. The initial culprits I wish to especially thank for my growth and development within FAST and the oil industry over the years are Professor Ken Sorbie, Dr. Myles Jordan, Dr. Gordon Graham and the sponsors of FAST, both past and present, who have always shown an interest in my research.

However over the years, all of the visiting Bésançon students and my FAST colleagues, who were forever changing, have also contributed to this process and a special thanks goes to Professor Ken Sorbie, Professor Eric Mackay, Professor Anne Neville, Mike Singleton and Robin Shields for their friendship, humour and support over the years. I feel great admiration for the Bésançon students who are young but full of eagerness to learn as they embark on their great adventure in Scotland with FAST. I thank them for the life they breathe into the group each year and into me as I work with them on their individual projects and share a snapshot of life with them. These memories live on with me long after they have gone and it is always refreshing to receive news from them after their departure. During my time with FAST at Heriot-Watt University there are always moments when you require the skills of computer experts, administration support especially Heather O'Hara and the ladies, Angela Nelson and Jill Prior in stores, so I would like to say that I have appreciated all their prompt help and discussions in my time of need. Thanks are also due to Jim Buckman who succeeded in teaching me how to use the ESEM and EDX equipment to photograph and analyse my research samples.

After a great number of years in research, undertaking a PhD has always been in the plan however both Professor Anne Neville and Professor Eric Mackay can be very persuasive at times and I thank them for their persistence at highlighting the peer reviewed papers route that a PhD was achievable for me. As second supervisor, Professor Eric Mackay has taken a great deal of interest in my PhD project and I am extremely grateful to him for reading my draft thesis, his constructive advice and the support and confidence that he instilled in me throughout the process. For suggestions of technical input, I have to thank Professor Ken Sorbie for all his guidance, brainstorming sessions and especially for his mathematical skills in developing models

which predicted my experimental data. For the grammatical corrections my partner, Alan and my father, Ron who I am sure will be happy and relieved to see that it is now completed.

Last but by no means least I am especially grateful for the patience and understanding shown by my partner Alan and children, Lauren and Iain who have had to live with my laptop set up in the living room for more than a year! My parents, Eileen and Ron, have been there for me during the years' highs and lows and for that I thank them for all their support and encouragement. I would like to thank my brother Kenneth, his wife Lorna and my two nephews, Cameron and Findlay for providing me with entertaining days away from my laptop which have helped keep me rejuvenated over the year. There are many other family members as well as good friends, close by and others in far off countries that I would like to thank for their kindness and warm wishes that have kept me going – you all know who you are!

ACADEMIC REGISTRY

# Research Thesis Submission

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| School/PGI: | INSTITUTE OF PETROLEUM ENGINEERING | | |
| Version: *(i.e. First, Resubmission, Final)* | FINAL | Degree Sought (Award **and** Subject area) | DOCTOR OF PHILOSOPHY BY PUBLISHED RESEARCH IN PETROLEUM ENGINEERING |

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## List of Thesis Publications

**Paper 1:** Graham, G.M., Boak, L.S. and Sorbie, K.S.: "The Influence of Formation Calcium and Magnesium on the Effectiveness of Generically Different Barium Sulphate Oilfield Scale Inhibitors", *SPE Production and Facilities*, Vol. 18, Issue No. 1, pp.28 - 44, February 2003.

**Paper 2:** Graham, A.L., Boak, L.S., Neville, A. and Sorbie, K.S.: "How Minimum Inhibitor Concentration (MIC) and Sub-MIC Concentrations Affect Bulk Precipitation and Surface Scaling Rates", *SPE Production and Operations,* Vol. 21, Issue No. 1, pp.19-25, February 2006.

**Paper 3:** Boak, L.S. and Sorbie, K.S.: "The Kinetics of Sulphate Deposition in Seeded and Unseeded Tests", *SPE Production and Operations*, Vol. 22, Issue No. 4, pp.442-450, November 2007.

**Paper 4:** Kahrwad, M., Sorbie, K.S. and Boak, L.S.: "Coupled Adsorption /Precipitation of Scale Inhibitors: Experimental Results and Modelling", *SPE Production and Operations*, Vol. 24, Issue No. 3, pp.481-491, August 2009 (Online 30th July 2009).

**Paper 5:** Boak, L.S. and Sorbie, K.S.: "New Developments in the Analysis of Scale Inhibitors", *SPE Production and Operations*, Vol. 25, Issue No. 4, pp.533-544, November 2010.

**Paper 6:** Shaw, S.S., Sorbie, K.S. and Boak, L.S.: "The Effects of Barium Sulphate Saturation Ratio, Calcium and Magnesium on the Inhibition Efficiency: I Phosphonate Scale Inhibitors", *SPE Production and Operations,* Vol. 27, Issue No. 3, pp.306-317, August 2012.

**Paper 7:** Shaw, S.S., Sorbie, K.S. and Boak, L.S.: "The Effects of Barium Sulphate Saturation Ratio, Calcium and Magnesium on the Inhibition Efficiency: II Polymeric Scale Inhibitors", *SPE Production and Operations,* Vol. 27, Issue No. 4, pp.390-403, November 2012.

*Note:*

- Some of the calcium work, not including the mechanistic evaluations of inhibition efficiency versus [SI] remaining in solution, reported in Paper 1 has previously been included as part of a MPhil Thesis submission by Lorraine .S. Boak
- The experimental work in Papers 6 and 7 has been previously included in a previous PhD Thesis by Scott Shaw
- The peer reviewed papers will not appear in chronological order in the critical review

## Investigations Undertaken

The following aspects were studied in this thesis;

- Systematic examinations of the effect of divalent ions, $Ca^{2+}$ and $Mg^{2+}$ on scale inhibitor performance - **Paper 1, 6 and 7**

- Bulk precipitation versus surface deposition studies over a range of temperatures – **Paper 2**

- Kinetics of sulphate deposition in seeded and unseeded tests lead to the refinement of safe working envelopes – **Paper 3**

- Static bottle tests were used to identify whether an adsorption or coupled adsorption/precipitation process occurred under specific conditions – **Paper 4**

- Analytical procedures were developed or improved – **Paper 5**

## Nomenclature

| | |
|---|---|
| [ ] | concentration |
| < | less than or below |
| > | greater than or above |
| $BaSO_4$ | barium sulphate |
| C18 | type of solid phase extraction cartridge |
| $CaCO_3$ | calcium carbonate |
| CAPEX | capital expenditure phase |
| CTP-A | cation ter-polymer A |
| CTP-B | cation ter-polymer B |
| DETPMP | Diethylentriamine penta (methylenephosphonic acid) – hexa phosphonate |
| DTPA | Diethylene-Triamine-Penta Acetic acid |
| DVLO | Dejáguin, Verwey, Landau, Overbeek Theory |
| DW | distilled water |
| EDTA | Ethylene-Diamine-Tri Acetic acid |
| EDX | electron diffraction x-rays |
| EPM | electron probe microscopy |
| ESEM | Environmental scanning electron microscopy |
| FAST | Flow Assurance and Scale Team |
| FEED | Front End Engineering Design |
| FW | formation water |
| HMDP | Hexamethylenediaminetetra (methylene phosphonic acid) – tetra phosphonate |
| HMTPMP | Bishexamethylene triamine penta kis (methylene phosphonic acid) – penta phosphonate |
| ICP | Inductively coupled plasma |
| IE | Inhibition Efficiency |
| Iso –SR | constant saturation ratio |
| -k | rate constant, $M^{-1}hr^{-1}$ |
| Ksp | solubility product |
| L | litres |
| LOQ | limit of quantification |
| LS | Low scaling |
| $M^{2+}$ | divalent cation i.e. $Ca^{2+}$ or $Mg^{2+}$ |
| MAT | maleic acid ter-polymer |
| mg/L | milligrams per litre |
| MIC | Minimum Inhibitor Concentration |
| MS | medium scaling |
| NACE | National Association of Corrosion Engineers |
| NaOH | sodium hydroxide |
| $NH_2$ | aminopropyl |
| nm | nanometer – a measurement |
| NSSW | North Sea Seawater |
| OMTHP | Octamethylene tetra amine hexa kis (methylene phosphonic acid) – hexa-phosphonate |
| OPEX | operating expenditure phase |
| OSRG | Oilfield Scale Research Group |
| P POLYMER | name of an ICP method used to detect phosphorous content |
| PFC | P-functionalised co-polymer |
| PHOS | name of an ICP method used to detect phosphorous content |

| | |
|---|---|
| PMPA | PolyphosphinoMethylated PolyAmine |
| PPCA | Phosphino PolyCarboxylic Acid |
| ppm | parts per million – a unit of concentration |
| PVS | PolyVinylSulphonate |
| QCMB | quartz crystal micro-balance |
| RDE | rotating disk electrode |
| SEM | scanning electron microscopy |
| SI | Scale Inhibitor |
| SI_Ca | scale inhibitor_calcium complex |
| $SiO_2$ | silicon oxide |
| SiOH | silicon hydroxide |
| Sp | Supersaturation, a measure of scaling tendency. Similar to SR |
| SPPCA | Sulphonated Phosphino PolyCarboxylic acid |
| Squeeze VII | Modelling software |
| SR | Saturation Ratio |
| $SrSO_4$ | strontium sulphate |
| SSA | specific surface area |
| SW | seawater |
| T | temperature |
| VS-Co | VinylSulphonated Acrylic Acid Co-polymer |
| Γapp | apparent adsorption |
| Π | precipitation |

## Table of Contents

# Chapter 1 Critical Review

## 1.1 Introduction to Scale and Associated Areas

Scale formation is one of the most problematic of a range of flow assurance issues within the oilfield industry (Vetter O.J. 1976; Weintritt D.J. 1967; Charleston, J. 1970). It has remained a problem over the years as conditions within well systems are constantly changing, hence scaling issues require significant consideration. Nowadays, one of the major factors in inorganic scale control relates to the design of production systems which has become significantly more complicated as the industry oilfields move from shallow water to deepwater completions involving subsea wells and long tiebacks. Intervention, required due to problems associated with co-mingling fluids from various tie backs, different sea water fractions and the physical and performance compatibility of other chemicals, becomes increasingly more costly, whilst correct placement of chemicals is challenging, hence the difficulty in managing scale increases (Graham, G.M. 2002c). In general, the further from the surface that scale forms, the more difficult it is to prevent or to remove it once formed. A higher quality of information available to aid any decision leads to a greater probability of success.

Scale formation can occur through two mechanisms; homogeneous and heterogeneous nucleation. Homogeneously formed scale particles do not necessarily deposit or grow onto a surface and hence, could flow through the system without causing too many depositional issues. However, the scale that forms by heterogeneous nucleation builds up on solid surfaces causing problems such as pressure increases and restriction of fluid flow in the formation, pipelines, surface facilities and can potentially prevent production equipment such as downhole sub-sea safety valves or the heat exchangers/motors on pumps from operating as illustrated in Figure 1. Deposition occurring in these locations relates to the local hydrodynamics (laminar/turbulent flow) and also to hot equipment surfaces, such as on the motor or heat exchanger of a pump, which encourage scale formation. The heat induces scaling to occur, thus preventing further heat loss, causing the pump to overheat and fail. Retrieval of the pump and the fitting of a replacement is an expensive exercise and this situation of inadequate scale prevention should be avoided (Jordan, M.M. 2000).

(a) (b) (c)

Figure 1: Photos of scale formation in (a) a removed pipeline (b) the separator and (c) clean separator

### 1.1.1 *Carbonate and Sulphate Scale Formation*

There are many different types of oilfield mineral scale deposits such as carbonates and sulphates. The most common of these scales are calcium carbonate and barium (or strontium or calcium) sulphate. However, other deposits can also form such as calcium or sodium naphthenates, asphaltenes, waxes, hydrates and exotic scales involving the sulphides of lead, iron and zinc or halides, which cause their own specific problems (Graham, G.M. 2000c).

Carbonate and sulphate scales are induced by different changes in conditions. For instance, carbonate deposits mainly form due to decreasing pressure and increasing temperature. These alterations in conditions allow the release of carbon dioxide from solution which increases the solution pH, causing carbonate scale to occur, Equation (1). The solubility of $CaCO_3$ decreases with an increase in temperature (Nancollas, G.H. 1985).

Calcium Carbonate Formation: $Ca^{2+} + 2HCO_3^- \Rightarrow CaCO_3 + CO_2 + H_2O$ (1)

The overall equation above, originates from the set of equilibrium equations below;

$CO_2\ (g) \Leftrightarrow CO_2\ (aq)$ (1a)

$H_2O + CO_2\ (aq) \Leftrightarrow HCO_3^- + H^+$ (1b)

$HCO_3^-\ (aq) \Leftrightarrow CO_3^{2-} + H^+$ (1c)

$Ca^{2+}\ (aq) + CO_3^{2-}\ (aq) \Rightarrow CaCO_3\ (s)$ (1d)

$H_2O \Leftrightarrow H^+ + OH^-$ (water) (1e)

Sulphate scales normally occur due to the mixing of incompatible waters, where one brine normally a formation water type contains barium ions and the other, a seawater type brine, contains sulphate ions, Equation (2). This sea water brine is normally injected to maintain well pressure, to allow continuous fluid flow required for production.

Barium Sulphate Formation: $Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} \Leftrightarrow BaSO_4\,(s)$ (2)

Equally equation (2) could occur for other divalent cations such as $Sr^{2+}$ or $Ca^{2+}$.

This precipitation of insoluble salt is due to the mixing waters creating a solution that is oversaturated with respect to salt content. The solution can no longer hold this amount of salt in the volume of water/liquid present. The ions that are incompatibility with each other form an insoluble complex which precipitates out of solution, as a solid. This scaling tendency of the fluid mixture changes with time depending on the ratio of seawater and formation water. For instance, Figure 2 shows a typical plot of scaling tendency and amount of precipitation for barium sulphate scale from the mixing of seawater and formation water during the wells life cycle (seawater injection).

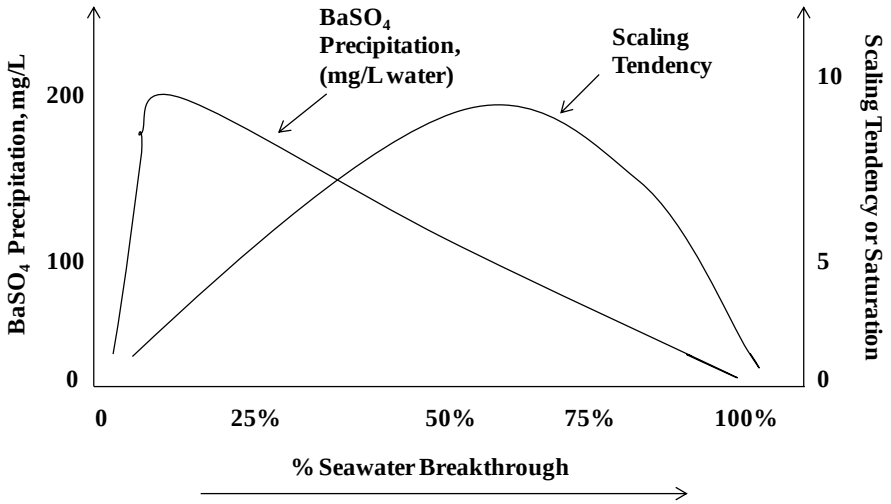



Figure 2: The scaling tendency and amount of precipitation for barium sulphate scale from the mixing of SW and FW during the wells life cycle (seawater injection)

Hence, this system has its maximum precipitation of barium sulphate occurring at a 10:90% SW:FW mix whilst the maximum thermodynamic scaling tendency, the driving force to reach equilibrium precipitation, is at a 60:40% SW:FW mix. An increase in

temperature reduces the scaling tendency. To inhibit scale formation, scale inhibitors operate through two different mechanisms; nucleation inhibition and crystal growth retardation. A lower concentration of scale inhibitor would be required to inhibit the maximum precipitation scenario than the maximum scaling tendency, as the scaling tendency is lower for the 10:90% SW:FW maximum precipitation conditions.

Scaling tendency can be measured in a number of forms; saturation index (SI), supersaturation (Sp) and saturation ratio (SR). The MultiScale thermodynamic prediction model, used in these studies, uses Saturation Ratio which is defined by Equation (3) as;

$$SR = \frac{[Ba^{2+}]_o[SO_4{}^{2-}]_o}{K_{sp}} \tag{3}$$

where $[Ba^{2+}]_o$ = initial barium ion concentration (mol/L); $[SO_4^{2-}]$ = initial sulphate ion concentration (mol/L); and $K_{sp}$ = barium sulphate solubility product, at temperature T, specific pH and ionic strength level. SR depends on a number of experimental conditions, including the SW:FW mixing ratio, temperature (T), pH, and ionic strength.

Over the years it has been acknowledged that scale prevention is better than waiting until the problem occurs and then taking remedial action. Usually, removal can incur considerable expense due to both the cost implications from mechanical clean-up but also the down time in production (Charleston, J. 1970; Jordan, M.M. 2000). Therefore, many different technologies have been developed over the years to reduce the risk of scale formation, control scale formation and to remove it if formed within downhole and topside oil/gas facilities. These technologies can now be considered for the CAPEX phase of a field's development in order that the costs and treatments are fully assessed both on land and offshore (Graham, G.M. 2004; Jordan, M.M. 2001; Simpson, C.M. 2005).

Carbonate scale has a higher solubility and can be removed far more easily by deploying an acid wash, compared with sulphate scale which has a very low solubility – 2.2mg/l. (Chemguide; Patroni Zavala, J.A. 2008). The solubility of $BaSO_4$ increases with an increase in temperature (20-100$^o$C) hence less precipitation occurs at higher temperatures. However, the reverse has been observed for $SrSO_4$ scale (Yuan, M.D.

1994; Nancollas, G.H. 1985). Scale dissolution studies normally use chelating agents such as DTPA or EDTA, depending on the scale type to be dissolved; barium sulphate (Dunn, K. 1999; Mendoza, A. 1999), calcium sulphate (Charleston, J. 1970) and a mixture of scales (Mendoza, A. 1999).

### 1.1.2 *Scale Prevention Methods*

Chemicals called scale inhibitors (SI) have, for many years, been the preferred downhole treatment for the prevention or control of scale formation and its subsequent deposition, by application in a 'squeeze' treatment (Vetter, O.J. 1973; Vetter, O.J. 1976; Sorbie, K.S. 1992b). In a squeeze treatment, a scale inhibitor is injected ('squeezed') through a producer into the surrounding near-well reservoir formation and then pushed further into the reservoir by a brine overflush. A pre-flush or spearhead may be injected prior to the main scale inhibitor injection to prepare the rock surface for the scale inhibitor package, Figure 3.

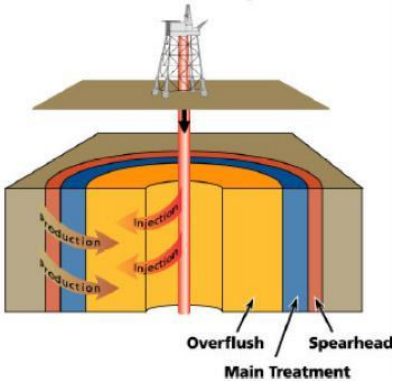



Figure 3: A schematic showing the scale inhibitor squeeze treatment process

There are two main scale inhibitor interaction processes that occur with the rock which allows the scale inhibitor to be retained in the formation; adsorption or precipitation. Adsorption is where the scale inhibitor is adsorbed from the solution onto the rock surface during injection and shut in. Precipitation is a time dependent process where the precipitation trigger is based on an increase in pH and temperature. After a shut-in period, production is resumed. For adsorption, the scale inhibitor will be desorbed gradually from the rock in order to give a slow return to the well at low but effective concentrations over a long period of time thus giving an extended squeeze lifetime. The precipitation return process is based on the solubility of the scale inhibitor-calcium complex formed and the dissolution rate in the localised area. Typical scale inhibitor field return profiles are shown in Figure 4.

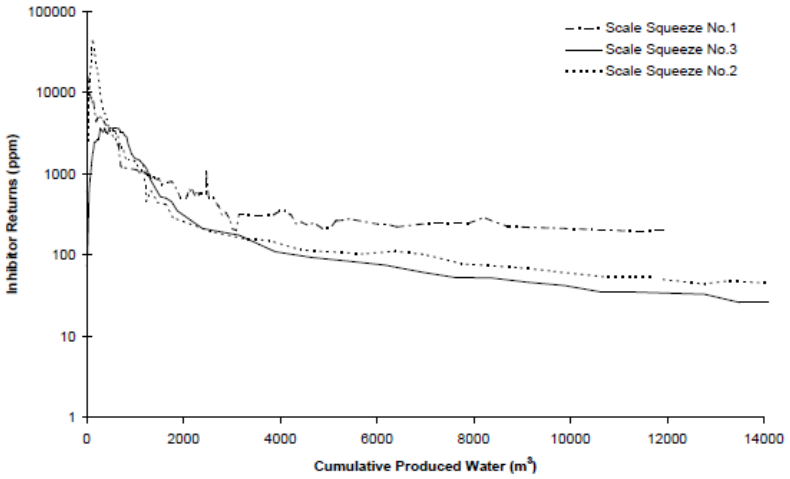



Figure 4: Typical field return profiles for the monitored scale inhibitor concentration (Mackay, E.J. 1998)

The structures of typical scale inhibitor species which could be applied during this squeeze process are shown in Figure 5.

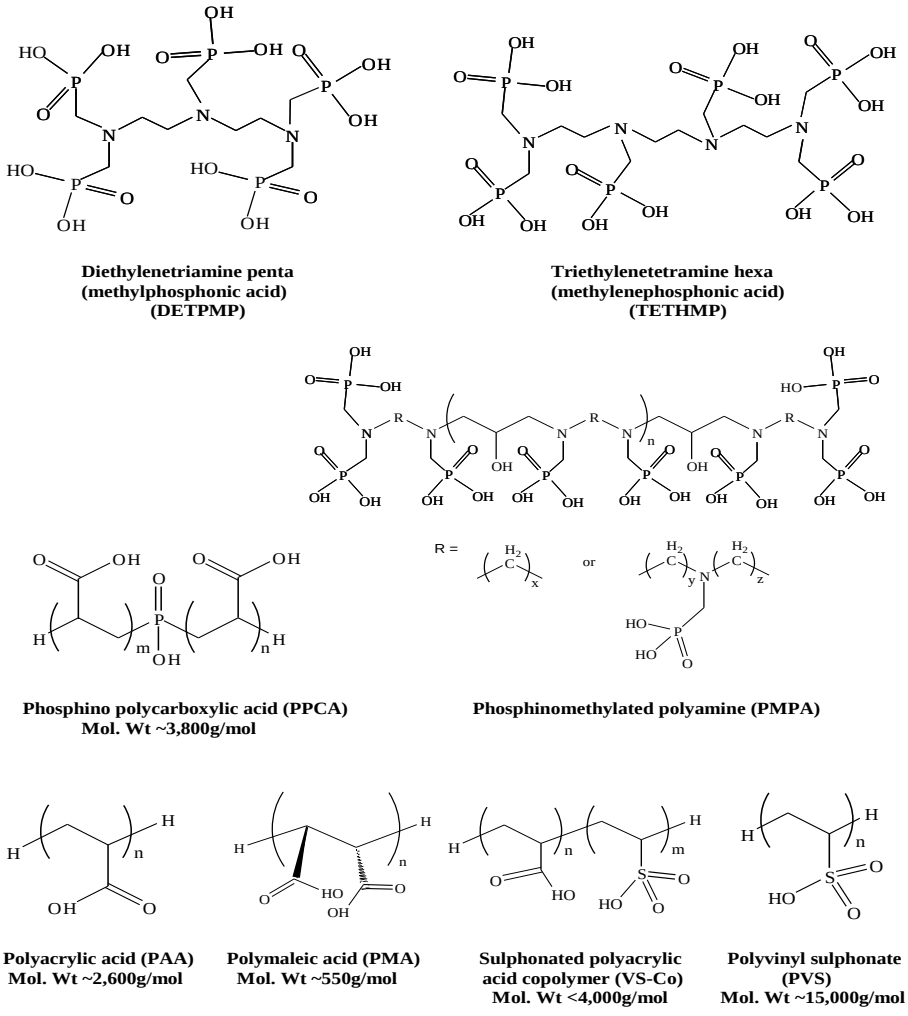



Figure 5: The structures of typical scale inhibitor species that could potentially be deployed in a squeeze treatment

With higher associated CAPEX, scale inhibitors can also be applied by continuous injection though downhole chemical injection lines. This protects the topside facilities such as the downhole safety valve and tubing above the packer, without interrupting production to apply the chemicals. (Cruise, D.S. 1983; Hustad, B.M. 2012; Ragulin, V.V. 2006). The technique is normally implemented when squeeze treatments would be difficult and costly to perform on a regular basis i.e. subsea wells. Criteria to consider are corrosion, chemical compatibility – brine/other chemicals/evaporation, particulate filters in place, temperature – chemical stability, chemical viscosity/pumping, other deposits i.e. hydrates and tubing material compatibility. In addition, the differences in chemical behaviour in a capillary instead of a bulk solution for similar conditions should be examined as they could potentially be significantly different leading to precipitation of chemical and corrosion issues in the downhole chemical injection lines (Goodwin, N.J. 2012; Olsen, J.H. 2011; Daminov, A. 2006).

Other workers have investigated the use of coatings or magnets to control scale formation. A low surface energy coating was found to have a lower amount of scale forming on it, however, once the first full covering of scale has formed then the surface energy has no impact on its formation (Wang, Z. 2005). Hence, the characteristics to make a surface more efficient need to concentrate on controlling the first layer of surface deposition. Consideration has to be given to a combination of surface chemistry, water/surface reaction, roughness, wettability, the shape of asperities and the brine and flow conditions being applied (Eroini, V. 2011). Whilst natural surfaces have been investigated (Cheong, W.C. 2008), fluoropolymeric materials of low surface energy and negative sticking tendency have been identified as suitable coatings (Lauer, R.S. 2007). They have been shown to be better than bare steel in preventing scale, when conditions representing a downhole tubular environment in the presence of oil were examined (McKeen, L.W.). Coatings are an advantage as no well-intervention is required, but if a coating becomes damaged then enhanced surface growth or corrosion may become a factor.

In the field of magnets, it has been stated that the magnetic treatment of fluids does seem to affect the scale precipitation; in terms of effects on nucleation and growth (Higashitani, K. 1993; Kronenberg, K.J. 1985) and crystallinity formed (Donaldson, J. 1988; Coey, J.M.D. 2000), but this is dependent on a wide range of parameters i.e. rate

of precipitation (Farshad, F.F. 2002), ionic load, magnetic configuration, contamination effects (Busch, K.W. 1986; Coetzee, P.P. 1998), interfacial effects (Gehr, R. 1995; Szkatula, A. 2002) and flow regimes. Most systems however, do depend on recirculation of fluids and not a once through system like an oil well, although there does appear to be a lack of a universally accepted mechanism. Hence, based on the evidence given, it cannot be recommended for controlling inorganic scales in long sections of tubing, although new products are emerging (Weatherford ClearWELL 2009-2010), but a potential application could be to protect high value equipment.

In addition, there are many other alternative options to scale inhibitor squeeze treatments which will be discussed in detail later on. All these techniques follow the general strategies for controlling scale, such as fluid modification, flow modifications, inhibition; however, if they are unsuccessful then scale removal is required.

Whilst using these techniques, other issues which require consideration are fluid temperature/pressure, chemical/fluid residence time in flow lines, impact of other flow assurance techniques, access to well and inhibitor placement. All these factors are important during a wells lifetime as each of these conditions will affect the performance of any chemical, scale inhibitor or other flow assurance products that enter the downhole or pipeline system. These effects may lead to an enhancement of the SI chemical's performance, but equally they may have detrimental effects. Therefore there is a requirement for an upfront risk assessment to gather information relevant to the well system in question, before any decision can be undertaken.

### 1.1.3 *Management of the Lifecycle*

Managing flow assurance issues and specifically scale formation means that nowadays there is an integration of resources at an early stage of field development to identify and manage the scale problem during the Capital Expenditure phase (CAPEX) rather than reacting to the problem once in the Operating Expenditure phase (OPEX) when the range of feasible options may be much reduced. Hence, operators are now planning well designs for new assets very carefully before a well is brought on line in order to optimally manage both the operating and financial aspects of the whole venture (Bogaert, P. 2007). This has been achieved by collating input from across disciplines such as reservoir engineering, production chemistry and completion engineering. This amalgamation of data gives a more complete assessment of scale risk and hence gives a

stronger indication of the correct economic selection of control program. This process is shown in flowchart form in Figure 6 (from Mackay, E.J. 2004, 2005). One type of decision made in the CAPEX phase of a development could be whether scale inhibitors via 'squeeze' treatments is a viable option or whether sulphate removal from the fluids would be more beneficial in the long term (Mackay, E.J. 2004). Each decision is not a standalone issue and a number of other factors and associated expenditure have to be considered (Graham, G.M. 1998) e.g. what is the severity of the scaling system? Are there divalent ions in the system that could aid the scale inhibitor's performance? Is the scale inhibitor thermally stable at the required reservoir temperature? Therefore, this is an extremely important decision process to follow as the specific conditions of a well can either enhance or detrimentally affect a SI chemical's performance. The operators rely not only on the wealth of historical or research knowledge that has been built up around the Petroleum Industry but also on various types of prediction models. These models help the operators to assess and visualise how each factor or condition would affect the wells production (Alwi, N. 2013; Chen, H.J. 2007; Guan, H. 2010; Mackay, E.J. 2003d). These prediction models cover a wide range of areas such as scaling potentials (Dai, Z. 2013; Petrotech 1998; Kan, A.T. 2012, 2013), kinetics (Tomson, M. B. 2004, 2009), amount of surface deposition, naphthenate formation (Murtala, M. 2010), where fluid flows within a reservoir (Mackay, E.J. 2003a, 2003b) and optimum volumes of treatments/overflush to use (Zhang, H.R. 1997), to achieve the longest squeeze lifetime.

Some of the areas mentioned in this introduction will be discussed further in Section 1.3 The Wider Industrial Picture. The main discussion will be based on scale inhibitors against barium sulphate scale. However, calcium carbonate will also be touched upon.

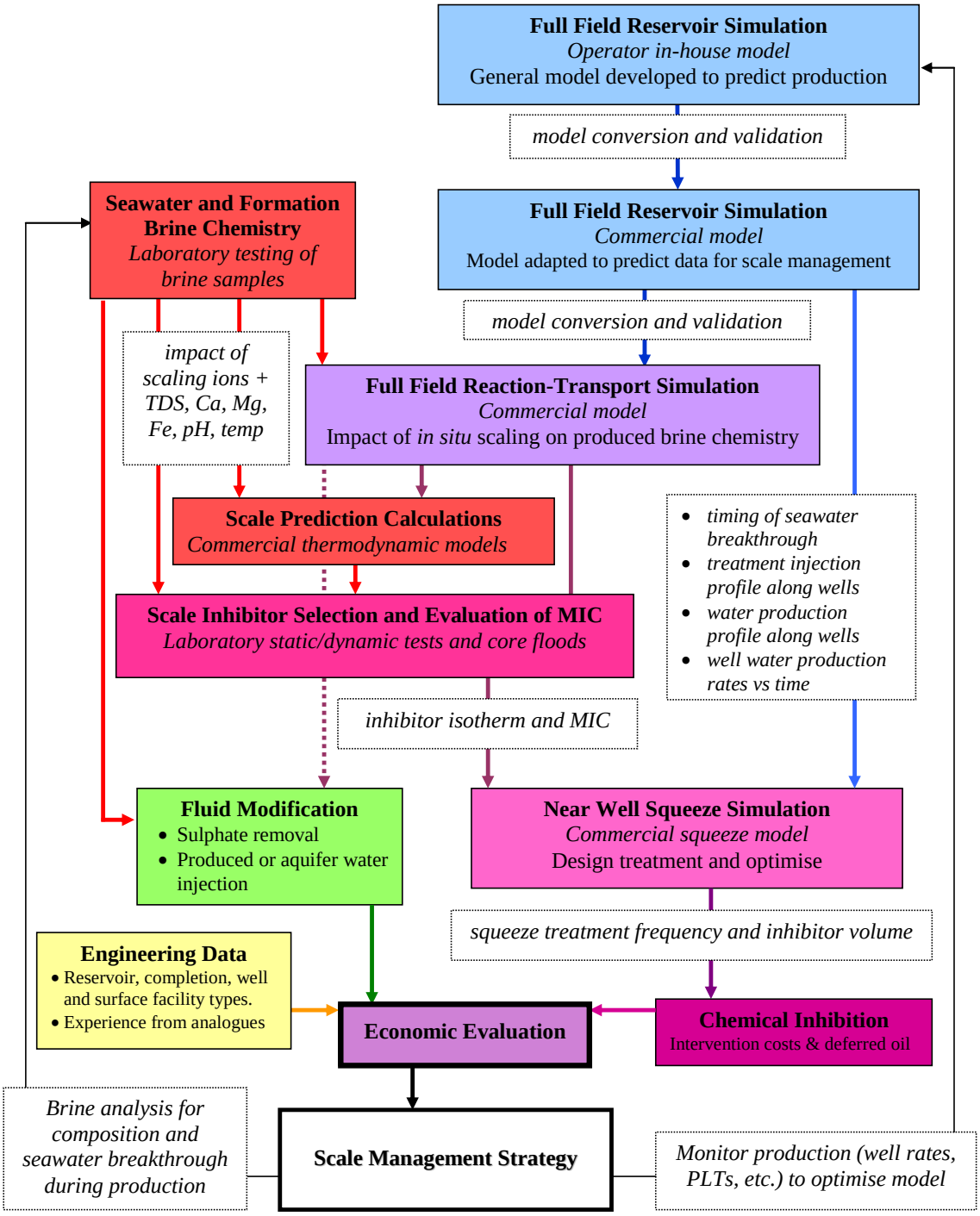



Figure 6: Scale management strategy selection process. The production chemistry stream is shown in red, and the reservoir engineering stream is shown in blue. These streams converge towards the end of the decision making process, to contribute towards the economic evaluation of the optimum scale management plan (Mackay, E.J. 2004, 2005)

## 1.2 The Aim of the Thesis

Scale inhibitors and several other chemicals which are introduced to protect against other flow assurance issues (e.g. corrosion, hydrate formation and wax deposition,

emulsion formation and bacterial growth), travel through the oilfield pipeline systems and encounter a wide range of physical conditions (T, P, salinity, hardness, pH etc.). Throughout their journey, all these chemicals are expected to work to the best of their ability. However, this can only be achieved if the mechanism through which these chemicals work can be fundamentally understood and quantified. The industry can then use this knowledge to assist in deciding which chemical would be the most appropriate one to be deployed depending on brine salinity, temperature, pH or rock mineralogy. Therefore the aim of this thesis is to contribute to the understanding of the fundamentals of how different factors impact scale inhibitor mechanisms. In addition, the oilfield industry can always benefit from advances in analytical techniques, to assay SIs, especially wet chemical methods to analyse emerging new products that are more environmentally friendly and hence contain less or no Inductively Coupled Plasma (ICP) detectable element.

The different factors and issues investigated in the experimental program carried out here were;

1. The effect of temperature;
2. The effect of the presence/absence of divalent ions in brines – specifically calcium and magnesium;
3. How inhibition efficiency (IE) performance relates to scale inhibitor concentration/inhibition mechanism and hence functional groups contained within the scale inhibitor structure;
4. Distinguishing between nucleation types i.e. homogeneous (bulk) versus heterogeneous (surface) and how the type of nucleation occurring affects the scale inhibitor concentration required to prevent scaling;
5. The effects of saturation ratio, ionic strength, $Ca^{2+}/Mg^{2+}$ ratio – Type 1 and 2 on the IE behaviour, for both phosphonate and polymeric species;
6. Incompatibilities with some polymeric species due to functional group precipitation with high calcium concentrations rendering their inhibition efficiency performance extremely poor against other species - Type A and B;
7. How the experiments and outcomes of the above are helped by numerous advances in wet chemical techniques for the assay of the scale inhibitor concentration, [SI], especially at very low levels around [SI] ~ 1ppm;
8. The effect of sulphate concentration on the kinetics of barium sulphate formation in a brine system;

9. The observations of any kinetic alterations if additional particles were introduced to a scaling system;
10. Whether it is adsorption or precipitation retention of the scale inhibitor within the rock porous media during a 'squeeze' treatment?

How each of these factors is investigated, is outlined in 1.2.2 Overview of Main Thesis Publications. How some of these factors were examined experimentally before the results were incorporated into prediction models will also be explained in this thesis.

### 1.2.1 *The Thesis Objectives and Methodology*

A number of experimental procedures were performed to try to achieve the overall aim, some of which used newly designed apparatus or alternatively, further developed previous methods/equipment to be more specific, in order to achieve more constructive results towards the desired aim.

For example, the standard NACE static inhibition efficiency (IE) performance test (NACE 1997) was used in Papers 1, 6 and 7 to evaluate the performance of scale inhibitors whilst varying the calcium and magnesium concentrations within the brine systems. This progressed to more systematic investigations of constant saturation ratio and fixed calcium/magnesium ratios which indicated the extent to which ionic strength influenced the SI performance. The introduction of a metal coupon setup in Paper 2 allowed surface scale deposition to be investigated alongside bulk scale deposition studies. These surface (heterogeneous nucleation) and bulk (homogeneous nucleation) scaling experiments allowed a schematic diagram to be compiled highlighting important zones to consider when performing or analysing the data from these types of experiments, over a wide temperature range ($5 – 95^{o}C$).

Another alternative to the standard NACE bottle test was the variation of adding additional particles (e.g. seed barite or sand) to the system in Paper 3, in order to observe any influence that these 'foreign' particles had on the kinetic rate of scale deposition. This in itself was no different to previous work performed by other researchers. However, the way in which the bottle tests were performed around a sulphate 'safe envelope' region further highlighted the importance of knowing the working system in order to maximise the observed effects. For instance, within a well, if faster scaling has occurred in the reservoir rather than in the production area, hence

causing a reduction in the scaling potential of the production fluids, then less scale inhibitor protection may be required in later life i.e. a lower than expected scale inhibitor concentration is required. One of the important outcomes of these tests was the enhancement of the sulphate 'safe envelope' by defining its associated error bars which will aid the industry to predict their scaling potentials and the mass of barite expected for specific brine systems.

Through the use of standard static adsorption tests in Paper 4 - varying the substrate mineralogy, pH values and scale inhibitor concentrations – the aim was to identify the percentage through which each mechanism – adsorption or precipitation – aids scale inhibitor retention in the rock formation. This would therefore allow a more appropriate 'squeeze' treatment to be designed, maximising its lifetime and potentially reducing the operator's costs.

The main analytical procedures followed during the investigations are detailed in full in Appendix A and are based on the procedures outlined in the Flow Assurance and Scale team (FAST) Laboratory Manual (Sorbie, K.S. 2006). The advances I made in Paper 5 for the wet chemical analysis techniques were in some cases completely new developments whilst others built on detection techniques already known, such as the Hyamine turbidity method. However, even these were implemented in a novel approach – e.g. by matrix matching or in conjunction with different cartridge types e.g. $NH_2$, thus achieving a less laborious procedure for sulphonated SI products. The ICP analysis for a non-aqueous solution was also a new achievement/procedure for FAST.

### 1.2.2 *Overview of Main Thesis Publications*

The importance of understanding the key fundamental factors that may influence scale inhibitor mechanisms are demonstrated and developed within seven main papers whose findings are the central technical basis of this thesis and are briefly listed below:

Systematic examinations of the effect of divalent ions, $Ca^{2+}$ and $Mg^{2+}$ on scale inhibitor performance - Paper 1, 6 and 7. In particular, these studies

- Examine inhibition efficiency performance
- Highlight two SI inhibition mechanisms; nucleation inhibition and crystal growth retardation

- Analyse the effects of constant saturation ratio (of barite), base and fixed calcium/magnesium ratios and ionic strength on different inhibitor species
- Rank the inhibitors into Type 1 or Type 2 categories depending on inhibitor behaviour and mechanism and into Type A or B depending on compatibility/incompatibility (i.e. no precipitate/precipitate formed) with high calcium concentrations (~1000-2000ppm)

Bulk precipitation versus surface deposition studies over a range of temperatures – Paper 2. This study

- Investigated a range of typical reservoir temperature conditions examined; 5, 50 & 95$^{o}$C
- Identified concentrations where enhanced surface growth occurs

Kinetics of sulphate deposition in seeded and unseeded tests lead to the refinement of safe working envelopes – Paper 3. This enabled us to

- Refine the error bar, around [$Ba^{2+}$] and [$SO_4^{2-}$] concentrations where little or no scale is expected to form – i.e. around a 'safe envelope'
- Examine kinetic effects when 'foreign' particles, such as barite or sand were introduced into the system
- Identify the appropriate residence times to allow the correct solubility product to be determined
- Enhance a previously developed model to allow more accurate 'safe envelopes' to be predicted

Static bottle tests were used to identify whether an adsorption or coupled adsorption/precipitation process occurred under specific conditions – Paper 4. In this study we

- Examined how to determine the fundamental mechanisms that may be occurring during a squeeze treatment
- Developed a model to potentially optimise scale inhibitor squeeze treatments

Analytical procedures were developed or improved – Paper 5. This allowed us

- To perform accurate analysis (+/- 5-10%) down to levels of order < 1ppm to allow precise analysis of squeeze return samples
- To identify less laborious techniques for sulphonated scale inhibitor species

- To analyse new products and achieve comparable results using independent ICP and wet chemical techniques, which is an advantage when different SI species are in the same co-mingled fluid and their individual concentrations need to be determined

A more detailed view of each publication is presented throughout this thesis and sets the context of how it contributes to the overall theme of this thesis and how it is relevant within the wider industrial picture. The analytical developments underpin the research work of the entire FAST group.

## 1.3 The Wider Industrial Picture

### 1.3.1 *Squeeze Treatments and Mechanisms of Inhibition*

Over the years, a vast amount of research and development work has been carried out on scale inhibitors (SI). SI's are applied downhole in the reservoir system in a 'squeeze' treatment (Vetter, O.J. 1973; Vetter, O.J. 1976; Sorbie, K.S. 1992b)). This process pushes the scale inhibitor into the reservoir formation in the near wellbore area where it propagates during an overflush stage of the squeeze treatment. The scale inhibitor is retained in the rock formation and a successful 'squeeze' treatment is when the scale inhibitor returns via the production lines at a low concentration, called a threshold concentration, over a very long period of time (the squeeze lifetime). This process was explained in more detail in 1.1.2. This life can typically vary between 1-12 months and a longer life is better however, this depends on what is defined as better. The main objective is usually to treat as many barrels of produced water, with the concentration of scale inhibitor remaining > MIC. This is more difficult, the higher the MIC and 'lifetime' in terms of actual time (days, months) is affected by the rate of water production of the well. The scale inhibitor is retained in the formation by adsorption or adsorption/precipitation mechanisms in which the scale inhibitor either desorbs or re-dissolves, in order to return to the production well. The released scale inhibitor protects the reservoir formation against scale formation and its subsequent deposition.

How these modes of interaction work for the scale inhibitor, is thought to be as follows;

(i) Nucleation Inhibition – Disruption of the thermodynamic stability of the growing nucleons (for homogeneous crystallisation). The mechanism of inhibition then involves

endothermic adsorption of inhibitor species, causing dissolution of the barium sulphate embryo crystals.

(ii) Crystal Growth Blocking – Interference/blocking of the growth processes of the growing crystals (for homogeneous crystal growth). The mechanism of inhibition then involves irreversible adsorption of inhibitor species at the active growth sites of the scale crystals, resulting in their blockage (Graham, G.M. 2000c).

These mechanisms can extend to heterogeneous nucleation where the scale formation occurs on surfaces such as a metal pipeline or equipment surfaces (Nancollas, G.H. 1985).

All scale inhibitors show an ability to work through both nucleation and crystal growth mechanisms. However, most species work predominantly through one of these mechanisms to achieve scale inhibition.

### 1.3.2 *Scale Formation: Homogeneous Versus Heterogeneous*

Scale crystals can form under heterogeneous and homogeneous conditions. Homogeneous crystal nucleation is most likely to occur in the bulk fluids of systems, such as in the standard laboratory bulk jar test. New crystals have to reach their critical nucleus size before they remain stable. However, as the stable barium sulphate nucleons gather together they form a barium sulphate crystal. These barium sulphate crystals will either have grown on a surface (heterogeneous nucleation) or remained in the bulk solution (homogeneous nucleation). If the barium sulphate crystals remain in the bulk solution and do not deposit/grow on a surface then they will flow through the system without causing too many problems. However, it is heterogeneous scale deposition which is more likely to occur in the field.

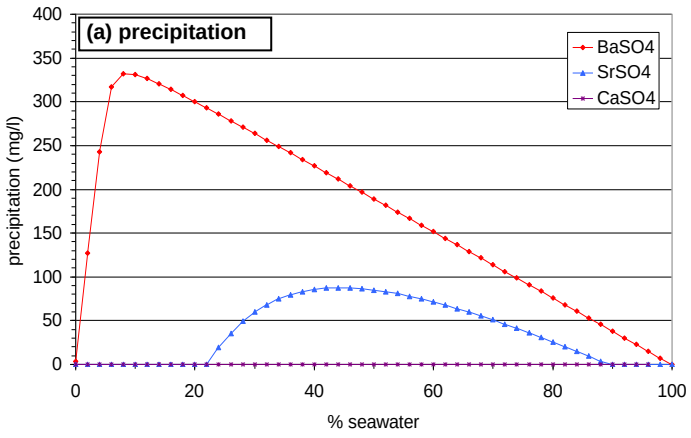
The nucleons/crystals formed via heterogeneous nucleation have a much shorter induction time as they grow and attach themselves to the many surfaces already present in the pipeline system such as in perforations, on tubulars, in valves and on previously formed scale. This nucleation process can be replicated in laboratory equipment such as in tube blocking rigs which test scale inhibitor performance against scale formation but under flowing conditions (Graham, G.M. 1997a, 2002a; Pritchard, A.M. 1988; Yuan,

M.D. 1998), or in surface deposition experiments where there is a metal surface present (Graham, A.L. 2004, 2005/2006; Graham, G.M. 2001a; Labille, S. 2001/2002).

The procedures for each of the above mentioned laboratory tests, surface deposition tests and the tube blocking rig, are well known (Sorbie, K.S. 2006). However, it is important that experiments should be run under conditions which are specific to the field conditions in question as the results from these types of tests can be dependent on temperature, pressure, pH and brine composition. All of these factors can influence the ranking outcome of the scale inhibitor species being evaluated. How the results are interpreted is of extreme importance (Graham, G.M. 1997a, 2002a, 2002c; Pritchard, A.M. 1988). Thermodynamic prediction packages are available; OLI ScaleChem™, ScaleSoftPitzer, MultiScale, allowing an insight into how a system is expected to behave, giving an indication of the scale type(s) that may be encountered, the severity of the scaling system and how much scale may be expected to deposit (Alwi, N. 2013; Chen, H.J. 2007; Guan, H. 2010; Mackay, E.J. 2003d; Petrotech 1997).

### 1.3.3 *Prediction Packages*

Mineral scale prediction software should be used to evaluate the scaling risk before any laboratory or field testing. The models highlight the appropriate mixing ratio and brine composition to investigate for the specific field conditions, by examining where the maximum supersaturation or where the greatest amount of precipitation may occur, Figure 7 (Yuan, M.D. 1994; Petrotech 1998).



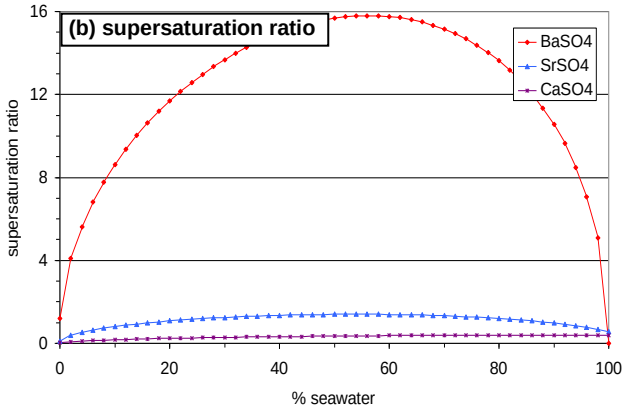



Figure 7: Comparison of (a) precipitation and (b) supersaturation ratio versus seawater fraction for sulphate scales at reservoir conditions (Mackay, E.J. 2004)

Sulphate scaling packages and geochemical models are recognised as being relatively accurate and various commercial packages have shown comparable results under well specified sets of conditions (Yuan, M.D. 1996; Bunney, J. 1997). However, accurate prediction of carbonate scaling is more difficult since it requires accurate data on downhole pH, [$HCO_3^-$] and saturation of $CO_2$ which are difficult to obtain (Kan, A. 2013). Scale prediction packages do, however, give qualitative information on the likelihood and severity of carbonate scaling and its profile throughout the lifetime of a particular field.

It is important to remember that water flow rates and compositions, and hence scaling tendencies, can change throughout the lifetime of a well. Changes in composition can be the result of dilution effects when brines mix in the reservoir, but in addition geochemical reactions in the reservoir can alter the composition of the brine by the time it reaches the production wells. These factors may affect the choice of how to manage the scale risk in the wells. Thus significant CAPEX cost decisions may be made depending on predicted brine compositions and produced water production rates. Errors in prediction of water production may impact timing of implementation of scale control measures, but also errors in brine analysis may impact the type of scale control measures chosen (Mackay, E.J. 2004) or even the type of chemical for the scale control (Graham, G.M. 2001c). Other packages have advanced scale prediction a stage further. For instance, more involved thermodynamic prediction programs (Collins, I.R. 2004, Petrotech, Mackay, E.J. 2002/2003c), reservoir fluid flow simulators (Mackay, E.J. 2003a, 2003b) and analytical models (Mackay, E.J. 2000) can be combined to assess the scaling risks throughout an entire group of reservoir wells, where they examine the

mixing of fluids and are then able to identify the severity and location of scaling problems, with and without reservoir stripping (Chekani, M. 2004; Mackay, E.J. 2000, 2003a, 2002/2003c; Petrotech). A major role is played by these models through identification of how different reservoirs and brine compositions react to specific conditions such as T and P; however, these calculations should be supported by laboratory studies using representative field conditions and kinetics. In fact one study using a predictive simulation model (Patroni Zavala, J.A. 2008) took experimental data and systematically examined the value of the amount of data taken from tests, and how it influences the predicted lifetime when experimental data points are removed from isotherm derivations, water production and injection profiles, flow profiles and the sampling frequency and duration of a core flood. The risk of not having sufficient data was evaluated against the required expenditure associated with the extra data collection. The extra data gave more accurate predictions and hence was worth the additional cost.

### 1.3.4 *Factors Affecting Scale Inhibitor Performance*

The inhibition efficiency performance of chemical scale inhibitors can be significantly affected by a number of factors e.g. environmental and chemical structures (El Attar Sofi, Y. 1990; Graham, G.M. 2001c).

The changes in environmental conditions could be pH, temperature, fluid hydrodynamics, the presence of other chemicals and brine composition. Factors such as brine supersaturation and the presence of divalent cations, such as $Ca^{2+}$ and $Mg^{2+}$ ions or even $Zn^{2+}$ (Kan, A.T. 2008), can lead to incompatibility between the brine system with the chemical, hence reducing its concentration in solution and its scale inhibition performance (Barthorpe, R.T. 1992; Boak, L.S. 1996; Cushner, M.C.1988; Dyer, S.J. 1998, 1999; Graham, G.M. 1997a, 1998, 2000; Shaw, S.S. 2010a, 2010b; Quddus, A. 2000; Yuan, M.D. 2001).

The interactions occurring between scale inhibitors and other chemicals, present in the system to combat other flow assurance issues, are also a major consideration (Graham, G.M. 2001b). For instance, both scale inhibitors and corrosion inhibitors are surface active chemicals, so there may be competition between the two chemicals for the surface that is present, which may in turn affect the performance of each (Boak, L.S. 2003; Graham, G.M. 2001b, 2002b; Labille, S. 2001/2002; Meric, C. 1985).

Chemical structure variations may occur as well. For example, they could be associated with molecular weight distribution of the scale inhibitor (Boak, L.S. 1996; Breen, P.J. 1990; Graham, G.M. 1994a, 1994b; Sorbie, K.S. 1992b; Van der Leeden, M.C. 1988a, 1988b/1990; Wilson, D. 1994) or with the functional groups present in the molecular structure of the SI such as a carboxylic or sulphonic acid grouping (Van der Leeden, M.C. 1982, 1988b/1990). These functional groups interact to block the crystal growth sites using dissociated or un-dissociated groups. Hence, pKa values of the chemicals are also important for different pH environments (Graham, G.M. 1997a; Griffiths, D. 1979; Howard, G.J. 1967; Ramsey, J.E. 1985). The position of the functional group in a chain structure is significant in that a functional group can be more effective if it is situated at the end of the chain rather than in the middle (Van der Leeden, M.C. 1988a). Each generic type of scale inhibitor can also have different binding affinities for these divalent cations that are present in the brine, quantified by the magnitude of the ligand metal binding constant (or stability constant) (Sorbie, K.S. 2004). Calcium and magnesium affinities with a penta-phosphonate species have been investigated in SEM/EPM studies (Boak, L.S. 1996; Graham, G.M. 1997b, 2003). A number of papers discuss the thermodynamic properties of organo-metallic complexes (Sawada, K. 1993; Dunn, W. 1999), chelating agents and their binding affinity to different metal cations such as alkaline earth metals, transition metals, etc. (Sanchez-Moreno, M.J. 2004), stability constants of phosphonic acids (Popov, K. 2001) and transition metal ions and their interaction with SI's (Kan, A. 2008). Binding between a scale inhibitor and divalent cations can have a major effect on the scale inhibitors' performance.

### 1.3.5 *Effect of Divalent Cations*

During a squeeze treatment, the calcium ion concentration in the produced or injected brine can influence the extent of a scale inhibitor being retained in the formation through adsorption or precipitation (Sorbie, K.S. 1993; Tomson, M.B. 2008). This is thought to occur through a number of surface/inhibitor complexation mechanisms all involving calcium ions. Binding between scale inhibitor and the scale crystal's growth sites or available surfaces, can occur through a number of mechanisms such as hydrogen bonding (~ pH2) or calcium bridging between the functional groups of the scale inhibitor and the surface or crystal (Sorbie, K.S. 1993) depending on the pH conditions. For instance, around pH 5 - 6, $Ca^{2+}$ is adsorbed onto the $SiO_2$ surface through the co-ordination of 1 $Ca^{2+}$ to 1 SiOH group displacing a corresponding hydrogen ion and its uptake is proportional to the surface area available, Equation (4),

$Ca^{2+} + SiO\text{-}H \Leftrightarrow SiO\text{-}Ca^{2+} + H^{+}$ (Iler, R.K. 1979) (4)

This surface bound $Ca^{2+}$ ion is then able to act as a bridge between the surface and the anionic scale inhibitor molecules, Equation (5),

$nCa^{2+} + (InH_{10-m})^{m-} \Leftrightarrow nCa(InH_{10-x})^{2n-x}) + (x\text{-}m)H^{+}$ (5)
(Carlberg, B.L. 1987; Oddo, J.E. 1990)

Higher pH, T and inhibitor concentrations favour the complexation between calcium and inhibitor (Barthorpe, R.T. 1992). In fact, phosphonates are known to be poor scale inhibitors at a low calcium concentration as the effectiveness of this type of scale inhibitor is controlled by the formation of $Ca^{2+}$/phosphonate inhibitor complexes. Such complexes are reported to inhibit either by promotion of nucleation (producing a sharp drop in supersaturation coupled with the formation of very small crystallites) or by the conventional crystal growth blocking mechanisms (His, C.D. 1992; Sweeney, F.M. 1993). Polymeric type inhibitors are effective at low $Ca^{2+}$ concentrations as they possess the ability to form multiple bonds between the longer macromolecules and the crystal surface, allowing stronger adsorption and in turn inhibition. In the presence of $Mg^{2+}$ ions, the performance of phosphonates is known to be significantly reduced whereas polymeric species are much less affected (Boak, L.S. 1999; Graham, G.M. 1992, 2003). The mechanisms through which these scale inhibitor complexes work to control scale formation is reflected in the efficiency performance of the scale inhibitor which has been related to the concentration of scale inhibitor remaining in the test solution at the corresponding residence time. (Graham, G.M. 2003). Inhibitor efficiency performance is defined as, Equation (6)

$$\text{Inhibition Efficiency (IE), \%} = 100 \times \frac{(C_I - C_B)}{(C_O - C_B)} \quad (6)$$

where; $C_I$ = concentration of barium at sampling time

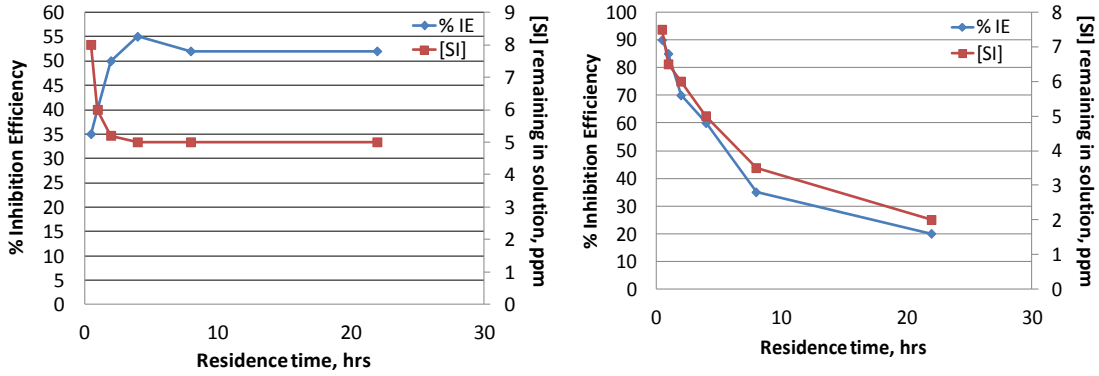
$C_B$ = concentration of barium in the blank solution (no inhibitor)

$C_O$ = concentration of barium originally in solution (i.e. at time = 0)

**Note:** $C_O$ is determined by adding the test NSSW and Forties FW to the KCl/PVS quenching solution in the appropriate ratio, as used for the quenched test solutions.

In general, the efficiency performance of a phosphonate type SI species is observed to be at a constant low level for all residence times (2 and 22 hours), which translated into mechanistic terms means that phosphonate species are less effective at preventing initial nucleation, Figure 8. However, once nucleation has started they are very effective at stopping further crystal growth by adsorbing at active growth sites on the mineral scale crystal lattice. The initial nucleation results in a drop in supersaturation which means the relatively high level of inhibitor remaining in solution is then sufficient to prevent further nucleation. Thus, after an initial drop in inhibition efficiency during the early (nucleation) period, they do not deteriorate very significantly because of this crystal growth inhibition mechanism.

The general inhibition efficiency trend for polymeric species tends to show high inhibition efficiency at early residence times but this drops off more gradually over time, Figure 8. From these observations it is suggested that small polyelectrolytes, such as polymers, operate primarily through a nucleation inhibition mechanism. Following initial nucleation, they continue to retard crystal growth, but do not appear to block growth completely and they therefore become less effective with time as they become consumed in the growing crystal lattice.




(a) (b)

Figure 8: A schematic showing the % inhibition efficiency against barium sulphate scaling versus the remaining scale inhibitor concentration in solution over a residence time of 22 hours (a) Typical crystal growth retardation behaviour and (b) Typical nucleation inhibition behaviour

For all generic types of SI species, this drop in inhibition efficiency is reflected by a corresponding drop in SI concentration at that residence time. (Graham, G.M. 1997a, 1997b, 2001a, 2003). This remaining solution SI concentration was monitored by ICP (Graham, G.M. 1995).

The morphology, composition, number and size of the barite crystals are affected when scale inhibitor is present, whether it is above, at or below minimum inhibitor concentration, MIC (Aoun, M. 1999; Graham, G.M. 2001a). This is due to the different inhibition mechanisms through which the generically different scale inhibitor species try to prevent both homogenous/heterogeneous (if a surface is present) scale formation.

***Paper 1: GRAHAM, G.M., BOAK, L.S. and SORBIE, K.S.: "The Influence of Formation Calcium on the Effectiveness of Generically Different Barium Sulphate Oilfield Scale Inhibitors", SPE Production and Facilities, Vol. 18, Issue No. 1, pp.28 - 44, February 2003.***

Some knowledge was already available about the interactions between different scale inhibitor types and divalent cations such as calcium and magnesium, as reviewed in 1.3.4 and 1.3.5. However, in this paper a much more systematic approach was undertaken in more manageable systems where the scaling reactions were not instantaneous and the mechanisms could be distinguished. Generic scale inhibitors PPCA, DETPMP and PVS were examined in the presence of varying calcium and magnesium concentrations in both a low (LS) and medium (MS) barium sulphate scaling brine system, as illustrated in Figure 9 and Figure 10.

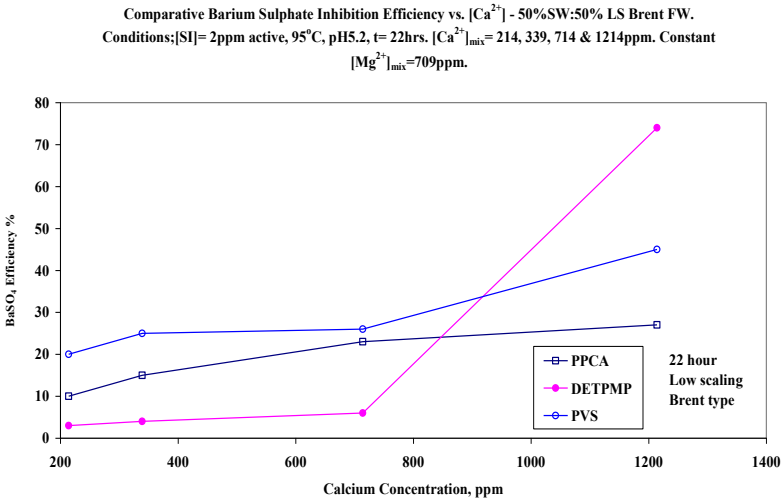



Figure 9: Comparative barium sulphate inhibition efficiency vs. $[Ca^{2+}]$ - 50%SW:50% LS Brent FW. $[Ca^{2+}]_{mix}$= 214, 339, 714 & 1214ppm. Constant $[Mg^{2+}]_{mix}$=709ppm

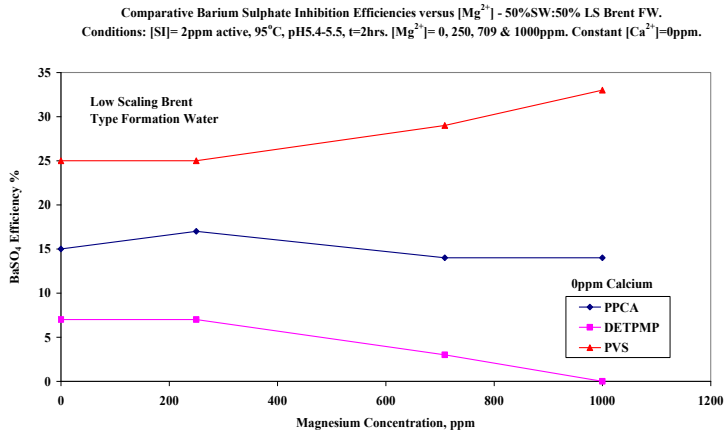



Figure 10: Comparative barium sulphate inhibition efficiencies versus $[Mg^{2+}]$ - 50%SW:50% LS Brent FW. $[Mg^{2+}]_{mix}$= 0, 250, 709 & 1000ppm. Constant $[Ca^{2+}]_{mix}$=0ppm

Trends from these static inhibition efficiency tests showed that inhibition performance is related directly to the affinity of the different scale inhibitor functional groupings to calcium cations, leading to improved performance. However, scale inhibitor interactions with magnesium led to detrimental changes in inhibition performance, for phosphonate type SI's such as DETPMP. A maximum inhibition performance was observed for a PPCA polymeric inhibitor at higher $Ca^{2+}$ levels in the medium scaling brine system. Compatibility tests confirmed this trend to be due to incompatibility between the PPCA and the brine causing the formation of a precipitate which reduced

the level of PPCA present in the solution. This in turn was observed as reduced scale inhibitor performance, as shown in Figure 11.

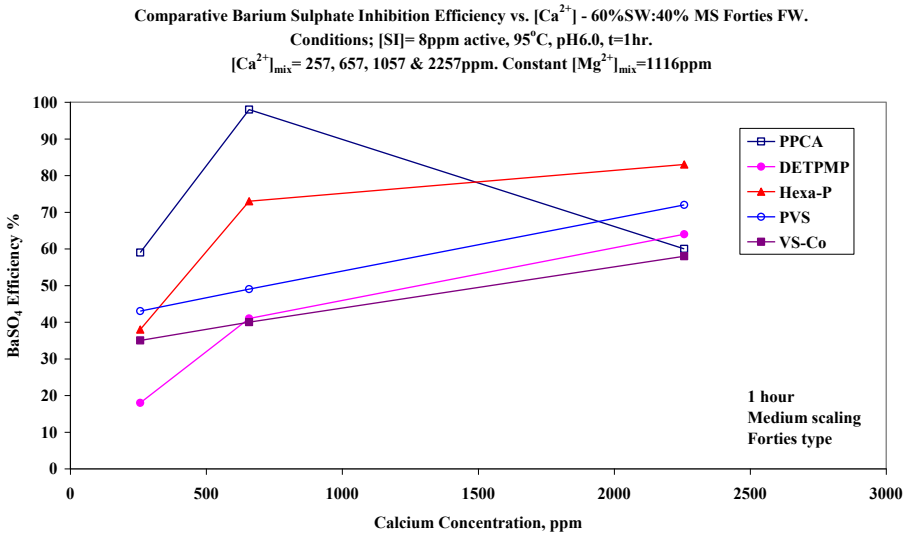



Figure 11: Comparative barium sulphate inhibition efficiency vs. $[Ca^{2+}]$ - 60%SW:40% MS Forties FW. $[Ca^{2+}]_{mix}$= 257, 657, 1057 & 2257ppm. Constant $[Mg^{2+}]_{mix}$=1116ppm

Using exceptionally high calcium concentrations and sulphate free seawater in the mixed brine to ensure no scaling was occurring, precipitates were formed for both PPCA and DETPMP which were examined using scanning electron microscopy for their morphology and electron probe microscopy was used to give their composition. The results from both indicated that the comparative affinities of different species for calcium and magnesium are markedly different, Figure 12.

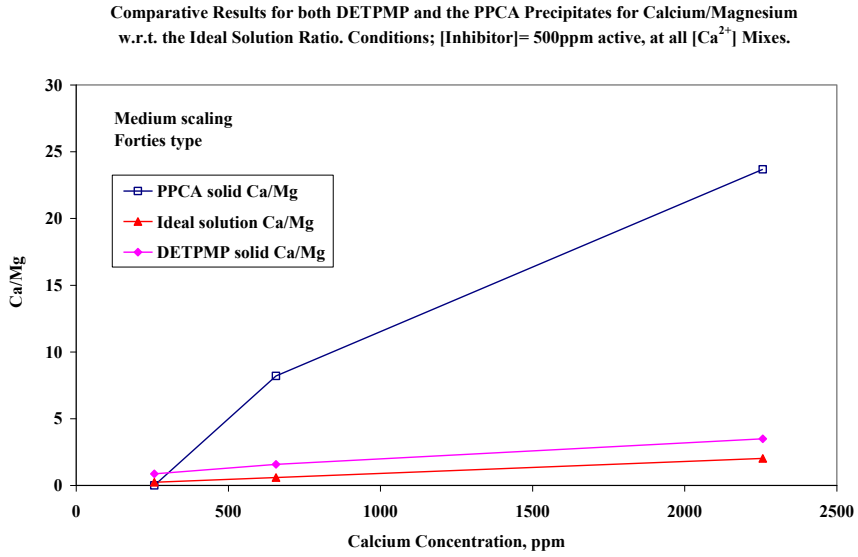
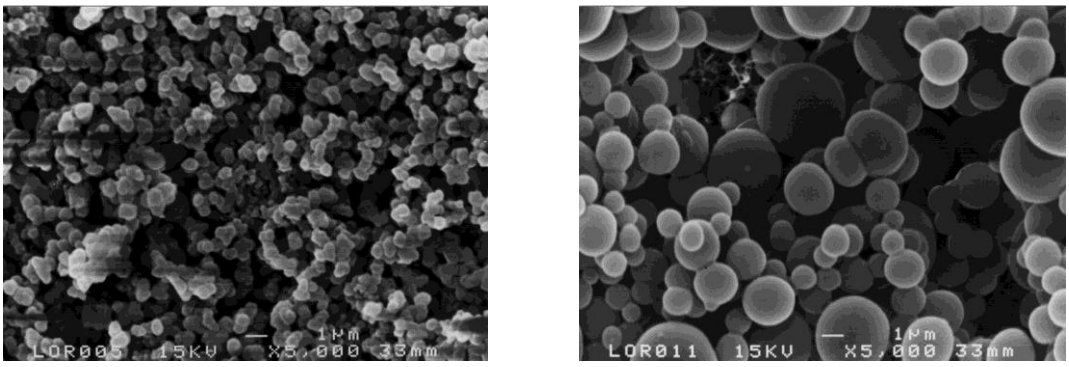



Figure 12: Comparative results for both DETPMP and the PPCA precipitates for calcium/magnesium w.r.t. the ideal solution ratio at all $[Ca^{2+}]$ mixes

The differences in the observed crystal morphologies were that the DETPMP particles, at all calcium levels, were always of a similar size, ~0.5μm and appeared to be joined to other particles, forming globule-type structures instead of single particles. In comparison, a large range of particle sizes were observed for the PPCA, and they were not joined but single in appearance. On average the PPCA precipitate particle size is larger than that observed for DETPMP. This size variation could be a function of the growth rate of the particles. For instance the DETPMP particles appear to be smaller and more abundant than the PPCA particles. Typical examples of the morphology observed for each SI are shown in Figure 13, for [SI] = 500ppm active at [$Ca^{2+}$] = 657ppm.




(a) (b)

Figure 13: SEM micrographs of the observed precipitate morphology from a compatibility test at [SI] = 500ppm active and [$Ca^{2+}$] = 657ppm, magnification x5000, (a) DETPMP and (b) PPCA

Mechanistic studies were performed comparing the manner in which polymers (PPCA) and phosphonates (DETPMP) absorb onto growing crystals and the inhibition performance with scale inhibitor concentration over the same time period was studied. This highlighted that PPCA inhibitors are good inhibitors at short residence times, up to 2hrs, but then decline in performance at longer residence times, as shown in Figure 14. In contrast, DETPMP gave a more constant level of inhibition following an initial drop in inhibition efficiency, Figure 15.

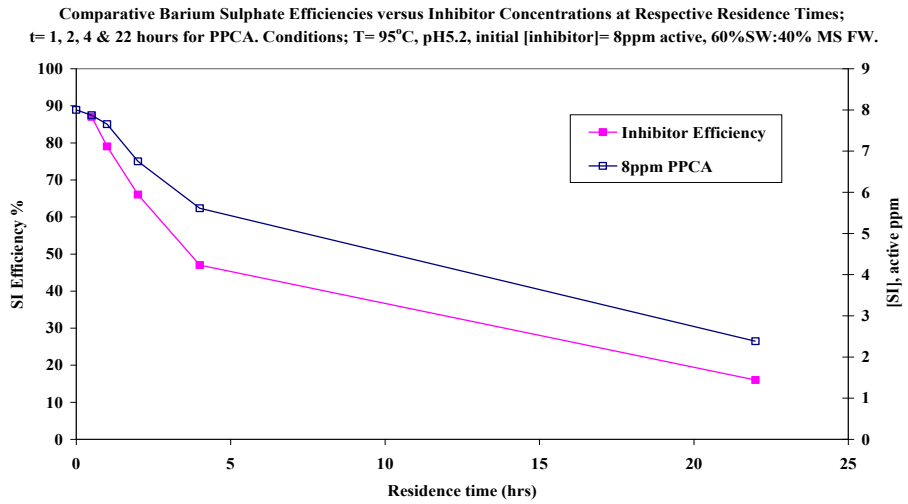



Figure 14: Comparative barium sulphate efficiencies versus PPCA concentrations at respective residence times - 60% SW: 40% Medium Scaling FW

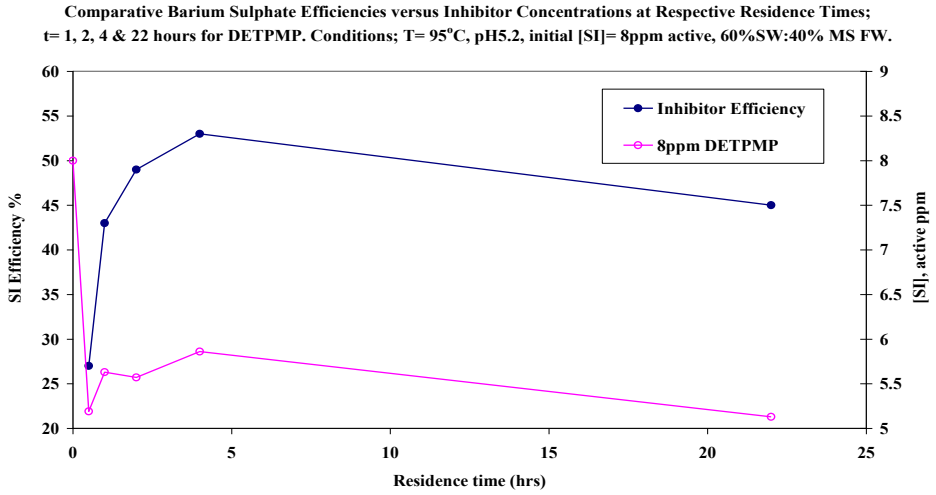



Figure 15: Comparative barium sulphate efficiencies versus DETPMP concentrations at respective residence times - 60% SW: 40% Medium Scaling FW

The inhibitor level present in the brine mixture, which results in, say 80% inhibition efficiency after 2 hours, may in fact be significantly lower than the original concentration. This finding may be one of the reasons why field MIC values are often found to be significantly lower in many cases than those determined in the laboratory.

Several types of experiment have been presented in this paper that help to further elucidate the mechanisms through which different scale inhibitors operate and in particular how the divalent cation level in solution affects this behaviour. This has

implications for two important but related areas, (i) testing different SI's for application in downhole and topside environments and (ii) on the choice of scale inhibition product in a produced brine in which the $Ca^{2+}/Mg^{2+}$ levels may vary (along with the scaling potential of the brine) during the production life of a field. This area has since been investigated in more detail in Papers 6 and 7 where a range of phosphonates and various polymeric species with differing functional groups in their structures are studied. The effects of saturation ratio, the $Ca^{2+}/Mg^{2+}$ molar ratio and consequently the ionic strength of the test brine with regard to their influence on the IE performance of all these inhibitor species were studied. Additional information was also obtained from this testing regime, with respect to the various crystal morphologies observed, the type of SI present and the influence of different functional groups on whether a polymeric species remains in solution and is able to work or if it precipitates, thus rendering the scale inhibitor species useless for IE.

***Paper 6: Shaw, S.S., Sorbie, K.S. and Boak, L.S.: "The Effects of Barium Sulphate Saturation Ratio, Calcium and Magnesium on the Inhibition Efficiency: I Phosphonate Scale Inhibitors", SPE Production and Operations, Vol. 27, Issue No. 3, pp.306-317, August 2012.***

From Paper 1 and other work (reviewed in Sections 1.3.4 and 1.3.5), it is known that the inhibition efficiency of barite scale inhibitors is affected by the presence of calcium and magnesium in the brine system and in addition also by the Saturation Ratio (SR) which was defined in Equation (3). The SR depends on a number of experimental conditions, including the NSSW:FW mixing ratio, temperature (T), pH, and ionic strength. All the tests in this paper examining phosphonate species were conducted at a fixed T= 95$^{o}$C and pH= 5.5, therefore only the brine mix ratio and ionic strength variables can affect the SR in the tests described here. The variation of SR with brine mixing ratio and ionic strength (i.e. base case vs. fixed case) is illustrated in Figure 16, for the brines in Table 1 and Table 2. It is well known that the MIC for barite prevention in a given brine mix increases with SR.

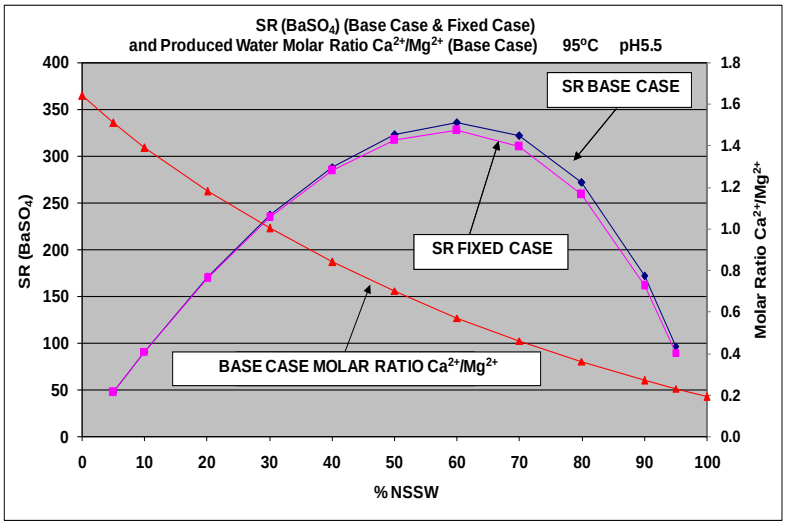



Figure 16: Barite Saturation Ratio, SR, vs. % NSSW for the base and fixed case experiments and the resultant base case brine mix molar ratio $Ca^{2+}/Mg^{2+}$ @95°C, pH5.5

| Ion | Concentration / ppm BASE CASE ($Ca^{2+}$ & $Mg^{2+}$ varying) NSSW | Concentration / ppm FIXED CASE ($Ca^{2+}$ & $Mg^{2+}$ fixed) NSSW | Concentration / ppm BASE CASE ($Ca^{2+}$ & $Mg^{2+}$ varying) Forties FW | Concentration / ppm FIXED CASE ($Ca^{2+}$ & $Mg^{2+}$ fixed) Forties FW |
|---|---|---|---|---|
| $Na^{+}$ | 10890 | 10890 | 31275 | 31275 |
| $Ca^{2+}$ | 428 | 0 | 2000 | * |
| $Mg^{2+}$ | 1368 | 0 | 739 | * |
| $K^{+}$ | 460 | 460 | 654 | 654 |
| $Ba^{2+}$ | 0 | 0 | 269 | 269 |
| $Sr^{2+}$ | 0 | 0 | 771 | 771 |
| $SO_4^{2-}$ | 2960 | 2960 | 0 | 0 |
| $Cl^{-}$ | 19773 | 15026 | 55279 | * |

Table 1: The brine compositions for Base case and Fixed case NSSW and Forties FW *refer to Table 2

| Mixing Ratio NSSW/FW | FW [$Mg^{2+}$] / ppm | FW [$Ca^{2+}$] / ppm | FW [$Cl^{-}$] / ppm |
|---|---|---|---|
| 20/80 | 924 | 2,500 | 56,702 |
| 60/40 | 1,848 | 5,000 | 63,819 |
| 70/30 | 2,463 | 6,667 | 68,563 |
| 80/20 | 3,695 | 10,000 | 78,053 |
| 90/10 | 7,390 | 20,000 | 106,520 |

Table 2: Fixed Case Formation Water (FW) $Ca^{2+}$, $Mg^{2+}$ and $Cl^{-}$ content

Many IE tests were performed in this investigation to examine: (a) a Base Case brine composition mixing North Sea Seawater (NSSW) and Forties Formation Water (Forties FW) where the $Ca^{2+}/Mg^{2+}$ molar ratio varied depending on the mixing ratio (Max SR at 60% NSSW, Max precipitation at 10% NSSW) and then (b) the influence of SR only on the phosphonate IE by fixing the $Ca^{2+}/Mg^{2+}$ molar ratio at 1.64 (2000ppm $Ca^{2+}$ and 739ppm $Mg^{2+}$ = 100% Forties FW levels in the mixed system). Additional information about ionic strength affects were gained when the $Ca^{2+}/Mg^{2+}$ molar ratio and saturation ratio were kept constant. Results were plotted for the recorded Minimum Inhibitor Concentration (MIC) for the specific IE test against % NSSW. A scale inhibitor concentration less than the MIC (previously determined) was used in all these tests so the effect of each variable is clearly visible.

Figure 17 and Figure 18 compare the behaviour of two penta-phosphonate type SI's at 2 and 22 hours residence time respectively, where the base case results with varying $Ca^{2+}$ and $Mg^{2+}$ concentrations are presented.

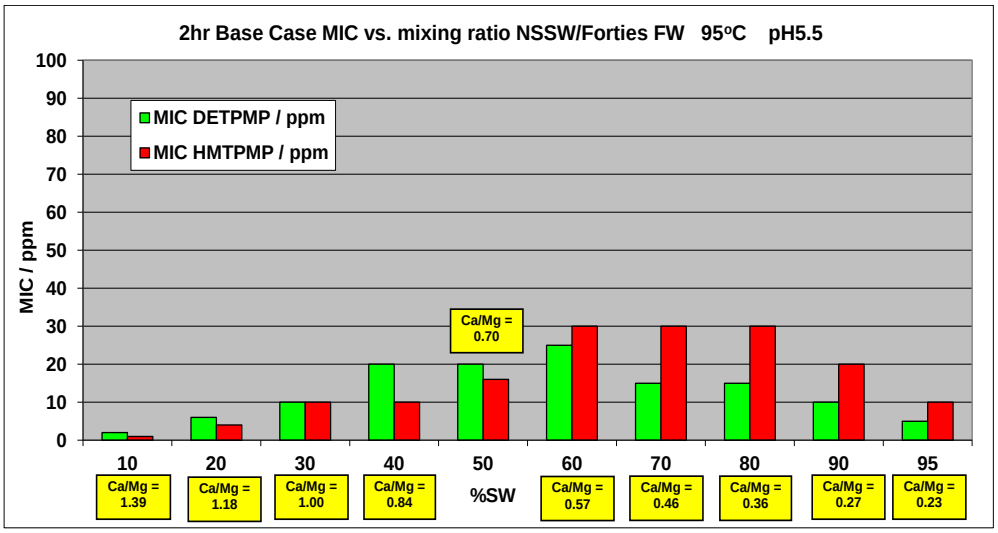



Figure 17: Base Case 2hr MIC values testing SIs HMTPMP and DETPMP vs. % NSSW @ 95°C, pH5.5

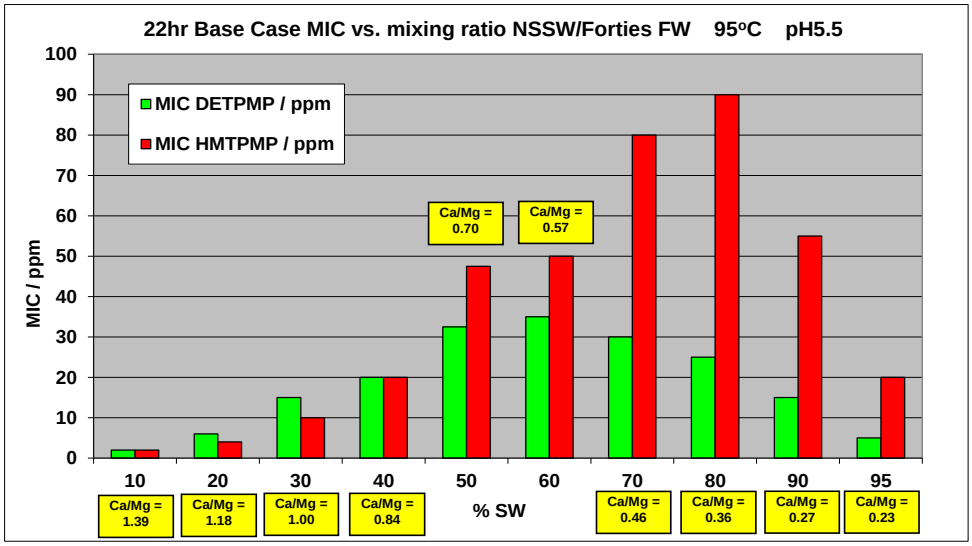
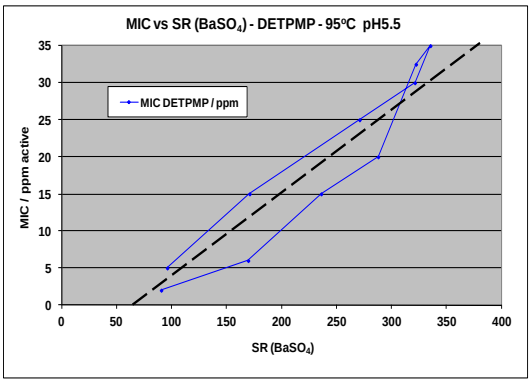



Figure 18: Base Case 22hr MIC values testing SIs HMTPMP and DETPMP vs. % NSSW @ 95°C, pH5.5

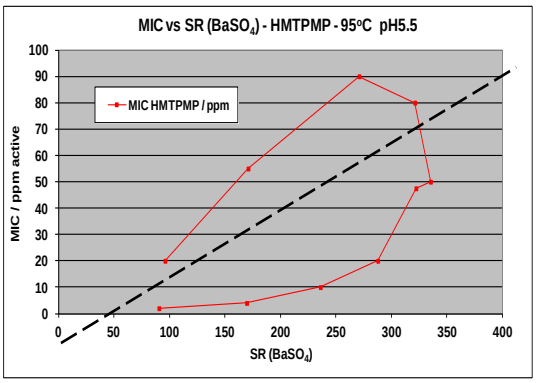
It can be observed from both Figure 17 and Figure 18 that the MIC vs. brine composition of the SI, DETPMP, correlates very well with SR, showing a clear maximum in MIC at 60% NSSW. Although HMTPMP shows some correlation with SR, higher MIC values are recorded at compositions above the maximum SR, especially at 22hrs. For example from Figure 18, the HMTPMP MIC value at 80:20 NSSW: Forties FW is ~90ppm, compared with an MIC of 50ppm at the max SR 60:40 NSSW: Forties FW. Hence, it is clear than an additional factor, to SR is operating and is significantly affecting the measured MIC for HMTPMP.

Other phosphonates, OMTHP (a hexa -phosphonate) and HMDP (a tetra -phosphonate) were tested and although the MIC levels of the two species are different, similar results are found to those for the penta-phosphonate tests, DETPMP and HMTPMP, where the MIC values of OMTHP follow SR whilst the MIC for HMDP increases to a max at ~80ppm for an 80:20 mix instead of ~50ppm at a 60:40 mix.

Hence, for two of the phosphonate species, DETPMP and OMTHP, the SR appears to be the primary control on MIC whereas for the HMTPMP and HMDP, the SR has some influence but there is clearly another factor operating. To confirm the correlation of SR with MIC, predicted SR values from MultiScale Software were plotted against MIC. Double values appear for lower and higher % NSSW as similar SR occurs at these mixes, Figure 19. Figure 19 shows the good (DETPMP) and bad (HMTPMP) correlation of SR with MIC, confirming the observed results.




(a) Good correlation




(b) Bad correlation

Figure 19: Plots of Base Case 22hr MIC vs. Barite SR for (a) DETPMP and (b) HMTPMP showing that the 22hr MIC values of the DETPMP correlate more closely with barite SR than HMTPMP suggesting another factor is influencing the IE of HMTPMP @ 95°C, pH5.5

From previous Paper 1 and analysing the process, it is believed that the $Ca^{2+}/Mg^{2+}$ molar ratio is the controlling factor here, as this quantity decreases in the base case brine system as % NSSW increases. Hence, a series of experiments was performed with a fixed $[Ca^{2+}]/[Mg^{2+}]$ of 2000ppm/739ppm giving a molar $Ca^{2+}/Mg^{2+}$ ratio of 1.64 (equivalent $Ca^{2+}/Mg^{2+}$ ratio in 100% Forties FW) in the mixed system independent of the brine mixing ratio being examined. The results from these tests, for DETPMP and HMTPMP, are illustrated in Figure 20 and Figure 21, at 2 and 22 hrs respectively.

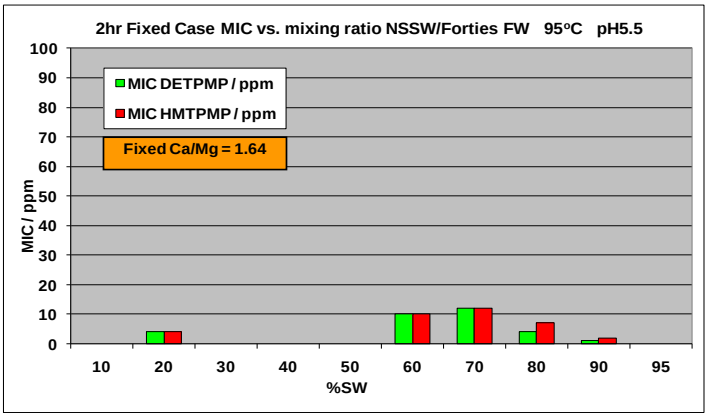



Figure 20: Fixed Case 2hr MIC values testing SIs DETPMP and HMTPMP vs. %NSSW at mixed produced water molar ratio $Ca^{2+}/Mg^{2+}$=1.64 @ 95°C, pH5.5

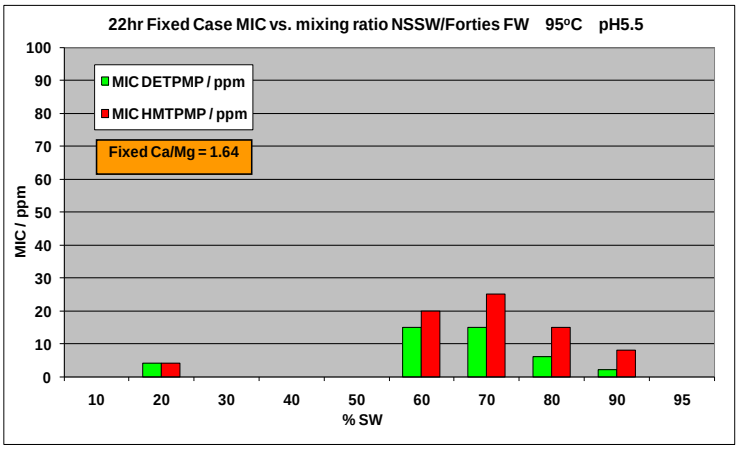



Figure 21: Fixed Case 2hr MIC values testing SIs DETPMP and HMTPMP vs. %NSSW at mixed produced water molar ratio $Ca^{2+}/Mg^{2+}$=1.64 @ 95°C, pH5.5

The 2hr comparison in Figure 20 for DETPMP and HMTPMP illustrates that the MIC values for each now closely agree and show a maximum at the same brine mix (70:30 NSSW:FW). For instance, the significantly higher MIC results recorded at greater % NSSW fractions observed in Figure 18, are not apparent here for HMTPMP. This is a strong indication that when the effect of $Ca^{2+}/Mg^{2+}$ molar ratio is controlled, then the MIC of HMTPMP depends principally on the SR of the brine mix. The 22hr results in Figure 21 show a similar trend although the actual MIC values for HMTPMP are higher than those for DETPMP. The results for the other phosphonates tested show similar behaviour.

An additional observation when comparing base case and fixed case experiments revealed that ionic strength, I, decreases with increasing % NSSW and this was a further variable in the experiments. The SR results in Figure 16 have indicated that ionic strength does not significantly affect the barite SR but it may potentially influence the IE of various SI. During this study it is believed that ionic strength does have a limited effect affecting the two 'pairs' of phosphonates differently. The results indicate that in the salinity or ionic strength range of these experiments, DETPMP and OMTHP have better IE performance at lower ionic strength and HMTPMP and HDMP perform better at higher ionic strength. For instance, from the Iso-SR results in Table 3, it is shown that the MIC for DETPMP at 20:80 NSSW: FW is 2ppm higher than at the 90:10 NSSW: FW mixing ratio. The converse is true for HMTPMP where the MIC is 3ppm lower at the 20:80 NSSW: FW than the 90:10 NSSW: FW mixing ratio. It is believed that it is this ionic strength effect that is still skewing the HMTPMP/HMDP results in

the fixed case, $Ca^{2+}/Mg^{2+}$=1.64 at higher % NSSW mixing ratios, i.e. in a lower ionic strength, but these phosphonate values work better in regions of high ionic strength.

| SI | Base Case or Fixed Case | 22hr MIC at NSSW:FW = 20:80 (ppm) SR =170 (bc); 169 (fc) | 22hr MIC at NSSW:FW = 90:10 (ppm) SR=171 (bc); 161 (fc) |
|---|---|---|---|
| DETPMP | Base Case ($Ca^{2+}/Mg^{2+}$ Varying) | ~7 | ~15 |
| HMTPMP | Base Case ($Ca^{2+}/Mg^{2+}$ Varying) | ~5 | ~55 |
| DETPMP | Fixed Case ($Ca^{2+}/Mg^{2+}$ Fixed) | ~4 | ~2 Lower *ionic strength* |
| HMTPMP | Fixed Case ($Ca^{2+}/Mg^{2+}$ Fixed) | ~4 Higher ionic strength | ~7 |

Table 3: Comparison of 22hr MIC levels for DETPMP and HMTPMP at different % NSSW compositions with approximately equal Barite SR values for the Base Case and Fixed Case

Although previously examined in Paper 1, further SI consumption tests were investigated here but this time for the different phosphonates. Typical trends for the % SI remaining in solution (from the initial dosed [SI]) and IE (%) vs. time are shown in Figure 22 and Figure 23 for DETPMP and HMTPMP respectively. It was found that DETPMP was not consumed into the barite/strontium lattice (i.e. removed from solution) as much as HMTPMP. The level of SI in solution broadly correlated with the IE at any particular sampling time. This relates to different Type 1 or 2 SI behaviours.

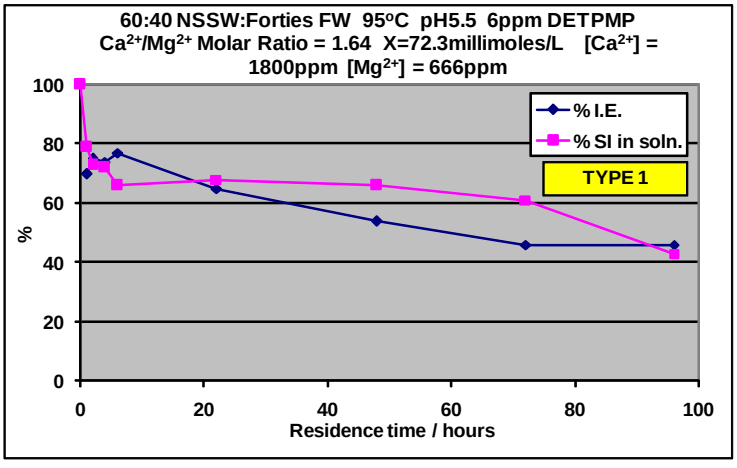



Figure 22: An illustration for the % IE and % SI in solution at various residence times for DETPMP. Conditions; $[SI]_{initial}$=6ppm, 60:40 NSSW: Forties FW with $Ca^{2+}/Mg^{2+}$ molar ratio = 1.64, $[Ca^{2+}]_{mix}$ =1800ppm, $[Mg^{2+}]_{mix}$ =666ppm; X=(moles $Ca^{2+}$ + moles $Mg^{2+})_{mix}$ = 72.3mM/L @ 95°C, pH5.5

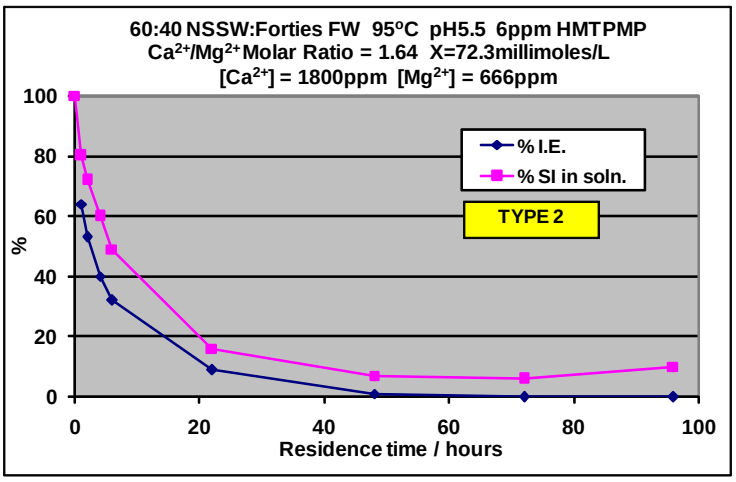



Figure 23: An illustration for the % IE and % SI in solution at various residence times for HMTPMP. Conditions; $[SI]_{initial}$=6ppm, 60:40 NSSW: Forties FW with $Ca^{2+}/Mg^{2+}$ molar ratio = 1.64, $[Ca^{2+}]_{mix}$ =1800ppm, $[Mg^{2+}]_{mix}$ =666ppm; X=(moles $Ca^{2+}$ + moles $Mg^{2+})_{mix}$ = 72.3mM/L @ 95°C, pH5.5

Environmental Scanning Electron Microscopy (ESEM) images of the scale deposits formed during these SI consumption/IE experiments were also captured. Figure 24 a-c show a typical set of images for (a) blank, (b) 8ppm DETPMP and (c) 8ppm HMTPMP in a barite/celestite scaling regime. As distinct morphology is observed for each, such SEM images could be used as a fingerprint to determine which type of phosphonate SI has been present in a static inhibition efficiency test.

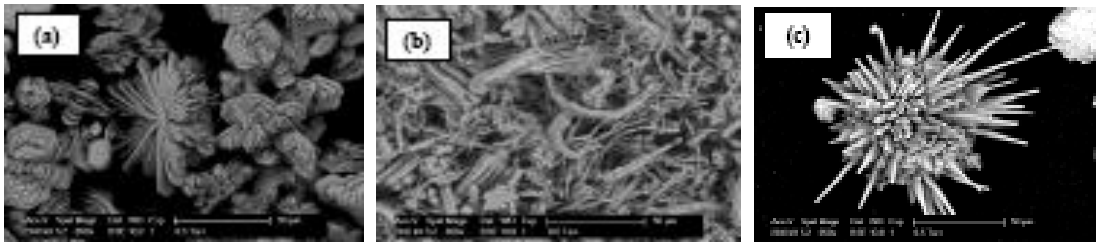



Figure 24 a-c: Examples of ESEM images at x650 magnification of typical barite/celestite precipitate formed in the presence of (a) No SI, a blank, (b) 8ppm DETPMP and (c) 8ppm HMTPMP

In all the experiments, the 'pairs' of phosphonates behave differently, therefore a classification of Type 1 can be used to describe DETPMP/OMTHP and Type 2 for HMTPMP/HDMP where Type 1 and 2 are described as below;

Type 1 – DETPMP/OMTHP

- Barite IE principally affected by barite SR
- Barite IE affected to some degree by brine $Ca^{2+}/Mg^{2+}$ molar ratio as a secondary effect ($Ca^{2+}$ assists and $Mg^{2+}$ 'poisons' inhibition of barite)
- Barite IE performance is better at lower salinities (for the ionic strength range tested here)
- IE tends not to decline very much with time i.e. IE at 2 and 22hrs is similar

Type 2 – HMTPMP/HDMP

- Barite IE is principally affected by brine $Ca^{2+}/Mg^{2+}$ molar ratio ($Ca^{2+}$ assists and $Mg^{2+}$ 'poisons' inhibition of barite)
- Barite IE affected by barite SR to some degree as a secondary effect
- Barite IE performance is better at higher salinities (for the ionic strength range tested here)
- IE tends to decline markedly with time i.e. IE much lower at 22hrs compared to 2hrs

Practically, it may be useful to deploy a Type 2 SI in high $[Ca^{2+}]$ reservoirs, since the IE of these SIs are enhanced by more $Ca^{2+}$ whilst Type 1 phosphonates are more appropriate for lower $Ca^{2+}$ production brines, but not too low a $[Ca^{2+}]$ otherwise the Type 1 SI IE performance will be detrimentally affected. A Type 1 phosphonate would be most appropriate for deployment in a reservoir of high $Mg^{2+}$ content since the IE of these species is suppressed much less severely by $Mg^{2+}$ compared to the Type 2 species. A blend of Type 1 and 2 would give synergistic benefits of both types of behaviour. In terms of monitoring squeeze treatments, it has been highlighted, from this study, that it is essential that both $[Ca^{2+}]$ and $[Mg^{2+}]$ should be monitored in the produced water and a $Ca^{2+}/Mg^{2+}$ ratio diagram should be plotted. Indeed, following this work, an operator in offshore West Africa (Chevron) has included such plots as a routine part of their data gathering. However, be cautious about selecting a scale inhibitor species on this Type 1 or 2 behaviour and MIC criteria alone as other additional factors should be considered, such as retention release for squeeze treatments, chemical cost and environmental impact etc.

***Paper 7: Shaw, S.S., Sorbie, K.S. and Boak, L.S.: "The Effects of Barium Sulphate Saturation Ratio, Calcium and Magnesium on the Inhibition Efficiency: II Polymeric Scale Inhibitors", SPE 130374, SPE International Conference on Oilfield Scale, Aberdeen, UK, 26-27 May 2010. Accepted for peer review publication in SPE Production and Operations, potentially November 2012***

In this paper, the effects of saturation ratio (SR) and molar $Ca^{2+}/Mg^{2+}$ ratio on the barium sulphate inhibition efficiency (IE) of nine polymeric scale inhibitor species (SIs) were investigated. These polymeric SI's were PPCA (Phosphino poly carboxylic acid), MAT (maleic acid ter-polymer, a green SI), SPPCA (sulphonated PPCA), PMPA (Phosphino methylated polyamine – a poly-phosphonate), PFC (a generic P-functionalised co-polymer), PVS (polyvinyl sulphonate), VS-Co (Vinyl sulphonate acrylic acid co-polymer), CTP-A and CTP-B (cationic ter-polymers A and B). The structures of the scale inhibitors not already previously shown in Figure 5 are given here in Figure 25.

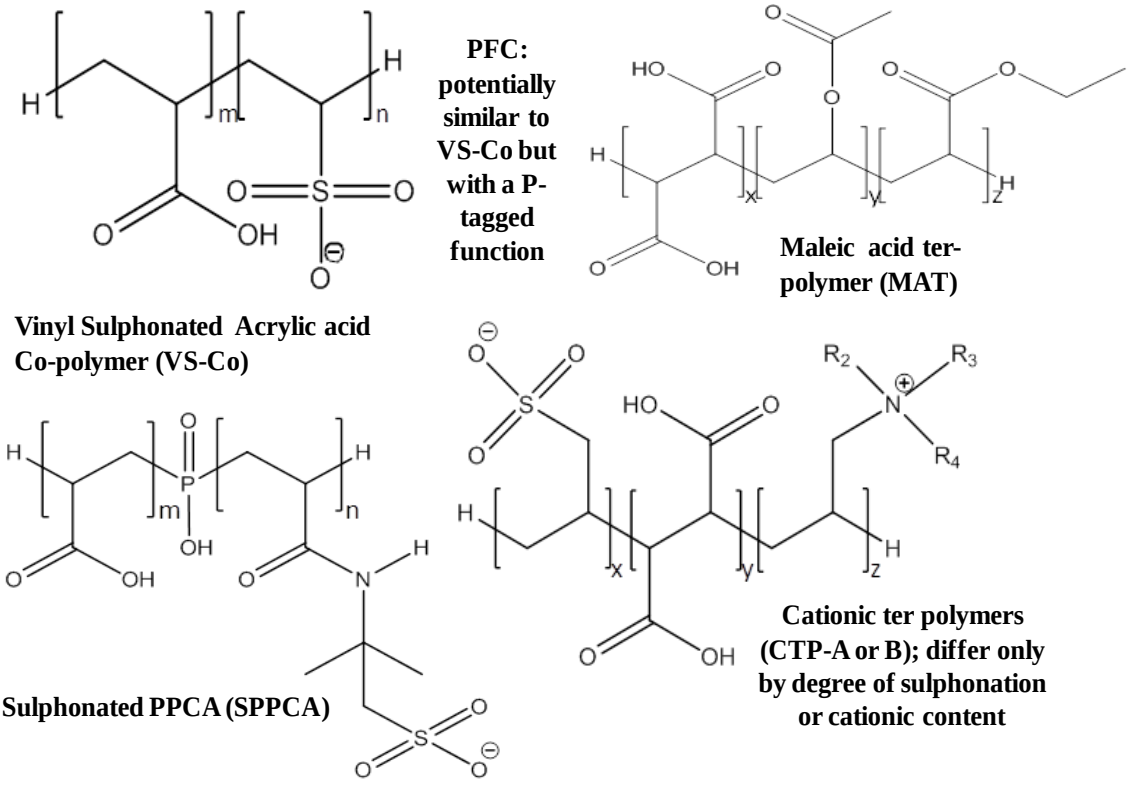
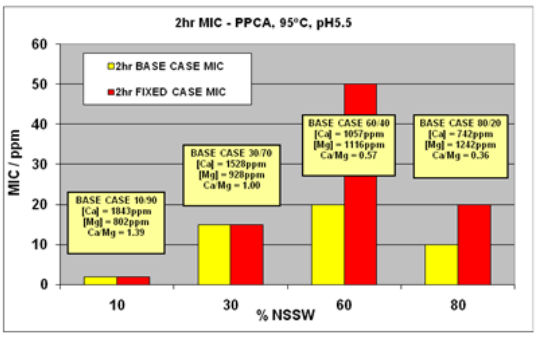
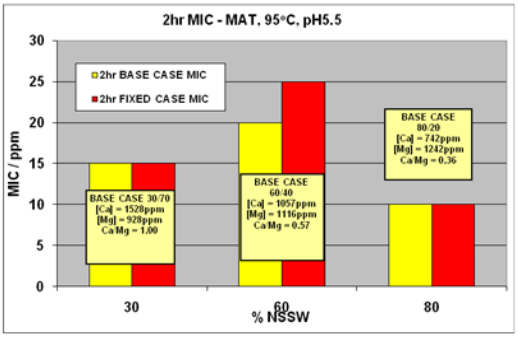



Figure 25: The additional SI structures for VS-Co, PFC, MAT, SPPCA and the CTP A and B

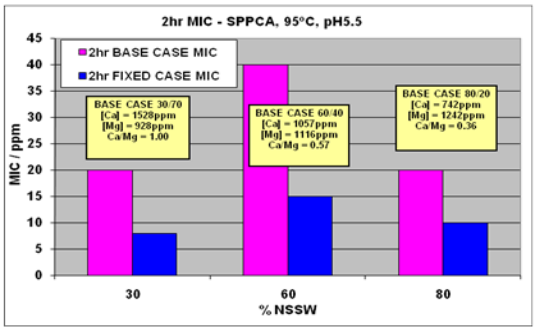
As with the phosphonates in Paper 6, IE experiments were performed for the polymeric products over a wide range of SW/FW compositions (i.e. SR and molar ratio $Ca^{2+}/Mg^{2+}$ varying). The Minimum Inhibitor Concentration (MIC) levels of these polymeric SIs were sometimes found to correlate with the level of SR; 60:40 MIC > 80:20 MIC > 30:70 MIC > 10:90 MIC, but not always. As with the phosphonates it was believed to be due to $Ca^{2+}$ and $Mg^{2+}$ effects. When the molar ratio was fixed, $[Ca^{2+}]/[Mg^{2+}] = 1.64$ then the MICs for all nine polymers studied correlated with SR levels, as illustrated for all 2hr results in Figure 26, for both types of IE test series. In addition however, it was observed that for SIs PPCA, MAT and PFC, the Base Case MICs (i.e. molar Ca/Mg ratio varying) were less than the Fixed Case MICs (molar ratio $Ca^{2+}/Mg^{2+}$ fixed); whereas testing SPPCA, PMPA, PVS, VS-Co and both the cationic ter-polymers, the converse is true i.e. Fixed Case MIC < Base Case MIC. This behaviour relates closely to the $Ca^{2+}$ and $Mg^{2+}$ levels in solution.



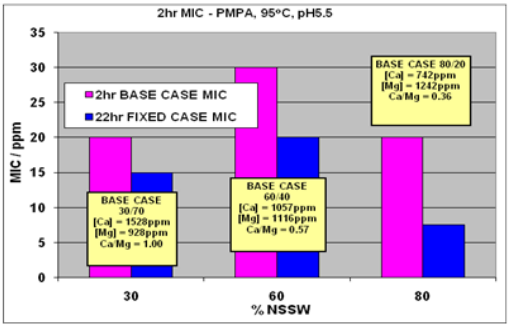

(a) PPCA



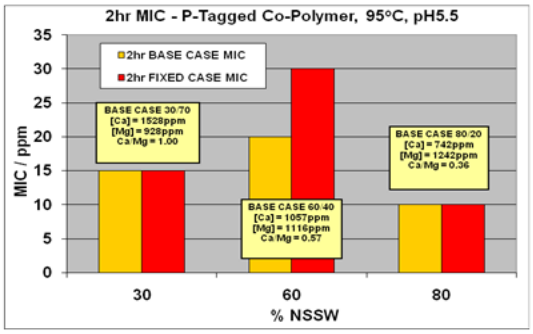

(b) MAT



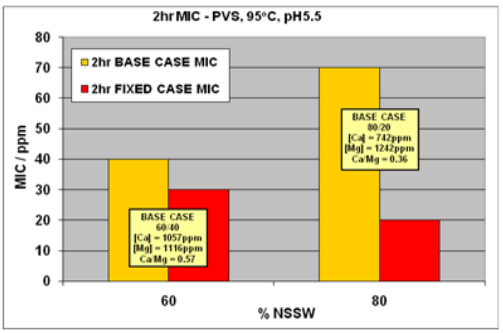

(c) SPPCA



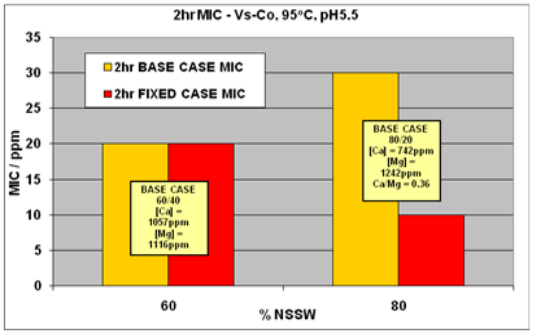

(d) PMPA



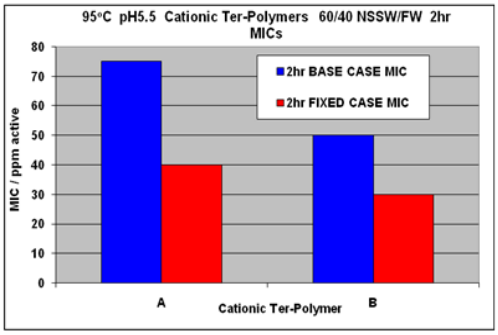

(e) PFC




(f) PVS




(g) VS-Co




(h) Cationic Ter-polymers

Figure 26 a-h: Plots of the 2hr MIC vs. % NSSW for SIs tested under both base and fixed case conditions @ 95°C, pH5.5. Similar trends at 22hrs.

From Paper 1, it is known that both types of scale inhibitor bind with cations however, at a certain calcium concentration ≥1000ppm there is an incompatibility with the polymeric species and $Ca^{2+}$ ions, rendering it ineffective against barite scale formation. Hence its inhibition efficiency performance significantly declines. This has been explicitly examined in this paper and results here confirm these findings. By examining the IE of PPCA at various molar ratios of $Ca^{2+}/Mg^{2+}$, a decline in IE was observed at a $Ca^{2+}/Mg^{2+}$ ratio = 5 after 2hrs and a $Ca^{2+}/Mg^{2+}$ ratio = 0.25 after 22hrs, Figure 27. The decline in IE is due to Ca-SI precipitation. Hence, after 22hrs, PPCA is still compatible when $[Ca^{2+}]$ = 644ppm and $[Mg^{2+}]$ = 1562ppm are in the system but optimum brine $[Ca^{2+}]$ will be dependent on test conditions. In addition, magnesium is shown to be detrimental; when no calcium is present and all the $X_m$ = 80.3 millimoles is magnesium i.e. $Ca^{2+}/Mg^{2+}$ ratio = 0 both 2 and 22hr IE are lower than when some calcium displaces magnesium i.e. $Ca^{2+}/Mg^{2+}$ ratio = 0.05. The 2hr IE improves by 20%, i.e. 70-> 90% and the 2hr MIC is achieved by just having 153ppm $Ca^{2+}$ present. This demonstrates that small changes in divalent concentrations can significantly affect the IE performance of scale inhibitors.

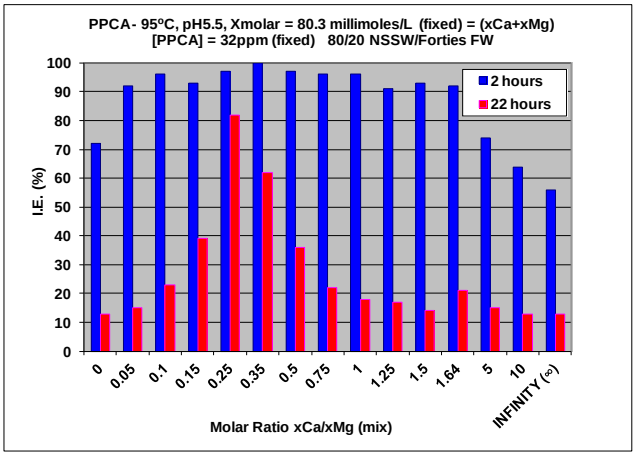



Figure 27: IE testing PPCA – varying molar ratio $Ca^{2+}/Mg^{2+}$ in the produced brine composition. $X_m$ (moles $Ca^{2+}$+ moles $Mg^{2+}$) = 80.3 millimoles/L is constant. Various molar ratios examined at [PPCA] = $32ppm_{act}$ – a pre-22hr MIC

Similar trends are found for the MAT SI, Figure 28, where higher calcium levels induce a decline in IE, although it is not as marked as for PPCA. This cannot be attributed to SI-Ca precipitation at this time, however, as it has not been fully tested. There could be another mechanistic reason for this.

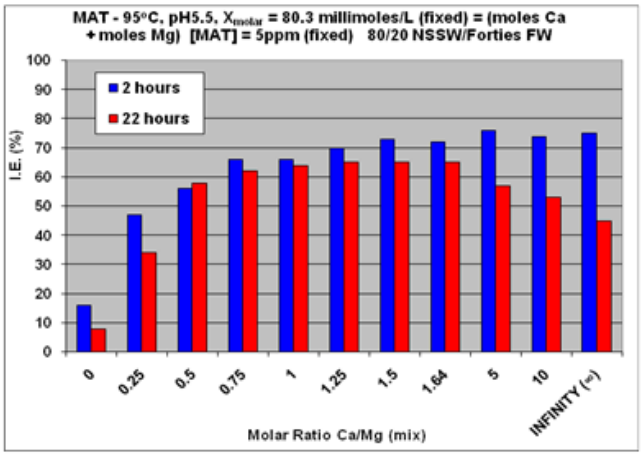



Figure 28: IE testing MAT – varying molar ratio $Ca^{2+}/Mg^{2+}$ in the produced brine composition. $X_m$ (moles $Ca^{2+}$+ moles $Mg^{2+}$) = 80.3 millimoles/L is constant. Various molar ratios examined at [MAT] = $5ppm_{act}$ – a pre-2hr MIC

The generic P-functionalised co-polymer PFC also exhibits the same sensitivity to the calcium and magnesium as PPCA and MAT. Although not presented here, PFC did undergo compatibility tests. A PFC-Ca complex was observed but with only 20-25% SI (cf. PPCA ~40%) being removed from solution and with slower reaction kinetics. This adds to the idea that poly-carboxylate type SI's may be susceptible to precipitation in

high [$Ca^{2+}$] brines. Now, PFC contains carboxylate groups and has some degree of sulphonation. By contrast the sulphonated PPCA, SPPCA, which like PFC, contains a p-tag and is carboxylated and sulphonated. However, it does not show any SPPCA-Ca incompatibility. For instance, from Figure 29, it can be observed that IE continues to increase over the whole range of $Ca^{2+}/Mg^{2+}$ molar ratios. This indicates that SPPCA continues to benefit from an increase in [$Ca^{2+}$] and does not precipitate as a SPPCA-Ca complex and hence remains effective against barium sulphate scale formation. Although not as obvious, due to a low level of SI being examined, a similar trend is observed for the 22hr data.

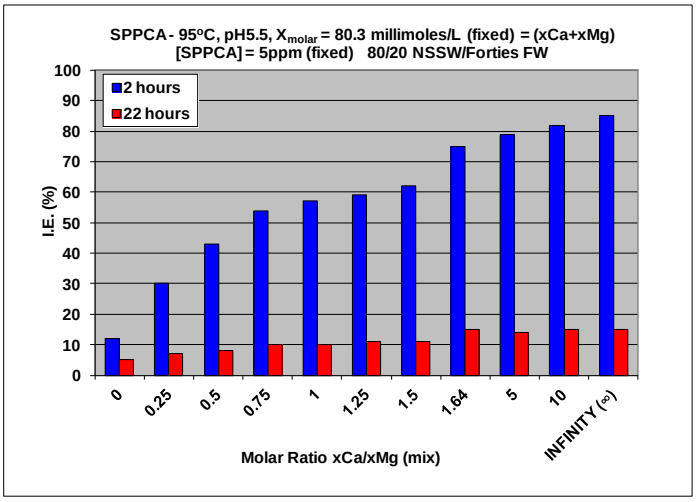



Figure 29: The 2 and 22hr IE of SPPCA vs. molar ratio $Ca^{2+}$/ $Mg^{2+}$ for [SPPCA] = $5ppm_{act}$ which is below the 2hr MIC

This difference in compatibility/IE behaviour, observed for 3 different types of SI, is thought to relate to specific differences in their structures. For instance, SPPCA is synthesised from acrylic acid (source of carboxylic acid functional groups) and AMPS side chains (source of sulphonate and amide-N-containing functional groups) monomer units and it could be the nitrogen atom $sp^3$ lone pair of electrons that can potentially form dative bonds with divalent cations, allowing it to remain in solution and not precipitate. The significant structural difference between the PPCA and MAT could potentially be the number of carboxylic acid functional groups (oxygen donor ions) present, with PPCA having more.

The synthesis of a SI such as a poly-phosphonate, PMPA (poly-nitrogenated and poly-phosphonated – many nitrogen atoms) was developed to capture the behavioural benefits of both polymeric (e.g. low pH applications) and conventional phosphonate SIs

(e.g. good retention). In contrast to PPCA and MAT, no incompatibility issues or loss of functionality with high [$Ca^{2+}$] are apparent for PMPA; indeed, the trend is remarkably similar to other Type 1 conventional phosphonates, although the MIC's are higher. In fact, recent evidence has indicated that PMPA may not be a polymer at all.

The majority of conventional phosphonates also contain nitrogen atoms in their main carbon chain e.g. OMTHP contains 4, DETPMP and HMTPMP contain 3 and HMDP contains 2. In fact, the abundance of nitrogen atoms in SI structures could be another factor influencing Type 1/ Type 2 IE behaviour (described in Paper 6). For instance, of those containing nitrogen atoms, PMPA may have a greater probability of exhibiting Type 1 IE characteristics due to additional $M^{2+}$-N dative bonding in addition to $M^{2+}$-O bonding via dissociated phosphonate or carboxylate function group oxygen donor ions.

Based on the 2 and 22hrs IE data for the polymers described in this Paper 7 and polymeric experimental results (limited data here), the polymers can be classed as Type 1 or Type 2 like the phosphonates (Paper 6). All of the polymers studied here can be classified as Type 2 (decline in IE with time), with the exception of PMPA – Type 1 i.e. high IE remains at 22hrs ~ 2hr IE. Again, this would be consistent with PMPA not being a polymer, as mentioned above.

In addition to the Type 1 or 2 designations, all SIs can now have an extra classification; Type A or Type B (compatibility/incompatibility with [$Ca^{2+}$] = ~1000-2000ppm+)

Type A – all phosphonates, SPPCA, PVS, VS-Co, CTP-A, CTP-B
Type B – PPCA, MAT, PFC

### 1.3.6 *Bulk and Surface Nucleation and Growth of Barite Scale*

Recently, the study and understanding of heterogeneous nucleation and growth has gained interest because scale deposition is recognised as a more important issue than homogeneous 'bulk' precipitation (Quddus, A., 2000; Graham, G.M. 2001a; Labille, S. 2001/2002; Morizot, A.P. 1999, 2000a, 2000b). Therefore, measures taken to reduce 'deposition' rather than bulk inhibition may reduce the risks in areas of the production system which are either difficult to access or where the cost of intervention is prohibitive, as may be the case in complex reservoir systems. Laboratory testing has therefore moved towards the more detailed study of surface deposition and the

development of new techniques which attempt to distinguish between homogeneous and heterogeneous nucleation (Morizot, A.P. 1999).

Some workers have investigated the use of electrochemical pre-treatment of metal coupons in a rotating disk electrode (RDE) set-up prior to testing in a calcium carbonate scaling experiment (Labille, S. 2001/2002; Morizot, A.P. 2000b, 2002). They demonstrated that the electrochemical pre-treatment of the metal RDE coupons can lead to effective surface inhibition of calcium carbonate. The presence of $Mg^{2+}$ ions during the pre-treatment enables a significant reduction in scale to be obtained. This is most effective when PPCA scale inhibitor is present, indicating that the $Mg^{2+}$ ions promote the ability of the SI to bind with the surface and develop an efficient inhibitor film which can retard further deposition. Two mechanisms of interaction were proposed in this work.

A similar electrochemical technique allowed the extent of scaling, for both $BaSO_4$ and $CaCO_3$, on a solid surface to be determined in the presence or absence of SI. It combined information obtained from scale formation at a solid surface with measurements of the solution (bulk) turbidity and amount of precipitation formed. Hence, a comparison could be made of the scaling kinetics on the surface and in the bulk solution (Morizot, A.P. 2000a). The efficiency of inhibition for both processes could also be assessed. The kinetics of the surface and bulk processes may be quite different for both types of scale. For example, enhanced growth of barite scale was found in the presence of SI at sub-MIC levels compared with an un-inhibited solution but was not found for $CaCO_3$.

Other studies also observed that certain conditions were particularly conducive to enhanced growth on a surface for barium sulphate (Graham, G.M. 2001a). These conditions arise when the scale inhibitor concentration present in solution is between zero (no SI protection), where barite should spontaneously precipitate and where the [SI] is at sub MIC levels. Above MIC, complete inhibition should be occurring and no barite should be forming. This enhanced surface barite growth, for [SI] < MIC, was thought to be due to the low level of scale inhibitor trying to control the faster homogeneous reactions in the bulk which allows the heterogeneous reactions at the surface to grow without interruption. Hence, this would lead to enhanced barite growth at the solid surface. For instance, there may be insufficient SI available to protect the

surface by film formation or the film formation is being influenced by other factors such as the calcium concentration in the brine system (Morizot A.P. 2000b, 2002).

The hydrodynamics, i.e. laminar versus turbulent, of the system also has a significant effect on the mass of barite formed on the surface (Boak, L.S. 2001; Graham, G.M. 2001a). More deposition has been shown to occur in a system which is laminar, than under turbulent conditions although more barite crystals may be formed under turbulent flow conditions than under laminar flow conditions. In laminar flow there is more time for the crystals to come in contact with the surface and grow there, whilst under turbulent flow conditions the crystals will be moving rapidly which does not allow the same amount of surface deposition to occur. However, this may be dependent on the precise design of the apparatus used for the experiment (Quddus, A. 2000).

The crystal alterations that occur in surface deposition can be observed using a number of techniques such as Scanning Electron Microscopy (SEM), Electron Diffraction X-rays (EDX) and Electron Probe Microscopy (EPM) (Graham, G.M. 2003; Liu, S.T. 1976). Whilst techniques such as in-situ monitoring, the Quartz Crystal Micro Balance (QCMB) and electrochemical impedance spectroscopy, can be used to monitor the surface deposition of scale (Chen, T. 2007; Gabrielli, C. 1997; Garcia, C. 1999). Other work has looked at surface nucleation and growth from a different perspective, using prediction models. For instance, the prediction and inhibition of surface scale growth has been quantitatively measured using Laser Raman Spectroscopy (Wylde, J.J. 2001) whilst Collins (Collins, I.R. 2002) used an extended DVLO theory to explain scale deposition behaviour on metal substrates and on modified metal surfaces which is shown to agree well with the limited experimental data available.

### 1.3.7 *The Kinetics of Barium Sulphate Scaling*

As with the performance of scale inhibitors, a number of factors also affect precipitation kinetics. These can be conditions such as brine scaling severity (the supersaturation), local hydrodynamics flow (laminar vs. turbulent), [SI] and temperatures (Aoun, M. 1999, Quddus, A. 2000). A clearer understanding of the influence of these various factors on the effective scale inhibitor MIC helps us to design around and compensate for reduced inhibitor performance.

One of the factors which can be examined very easily under lab conditions is temperature variance. Any differences in precipitation kinetics or scale inhibitor performance can be observed when a range of temperatures are examined – 5, 50 and 95$^{o}$C (Graham, A. L. 2005/2006; Sorbie, K.S. 2004; Yuan, M.D. 2001). The performance of scale inhibitors is greatly affected by temperature. For example, polyvinyl sulphonated (PVS) products work particularly well at low temperatures (T= 4$^{o}$C) whereas under certain conditions phosphonate type scale inhibitors appear to have a "switch on" temperature of ~70$^{o}$C i.e. they only start to perform satisfactorily at threshold levels above this temperature (Sorbie, K.S. 2004). However, this is not always the case under widely varying experimental conditions. For example, within a TBR system, DETPMP has been observed to show more retardation of $BaSO_4$ scale deposition at a lower temperature than at a higher temperature, contrary to static inhibition tests for the same brine system (Yuan, M.D. 2001).

Previous work has shown that scale kinetics and inhibition data from bulk precipitation are not always directly transferable to surface processes (Graham, G.M. 2001a; Hasson, D. 1996). For instance a higher [SI] is required to control surface scaling under the same bulk conditions (Morizot, A.P. 1999). However, although an increase in SI concentration, from zero to > MIC, increases bulk inhibition efficiency performance, this increase in performance does not translate to the inhibition of surface scaling. From one of our studies of surface deposition, a schematic diagram was constructed (Figure 30) to identify all the different zones encountered within the bulk/surface scaling test (Graham, A.L. 2005/2006). An area of enhanced surface growth was highlighted. Figure 30 should be investigated for individual systems in order to identify the danger zones that have to be protected with an additional squeeze treatment.

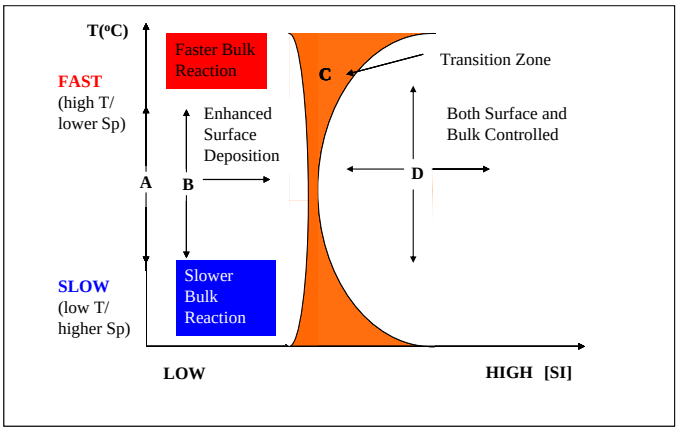



Figure 30: Schematic diagram of regions of surface and bulk scaling relative to [SI] and T ($^{o}$C)

Further work has investigated a flowing kinetic system using a flow cell which can be modelled as a stirred tank reactor (Boak, L.S. 2007b). Using this experimental approach with lower supersaturated brine systems allows slower kinetic rates to occur over longer periods of time. This allows us to study continuous surface growth and bulk deposition, such as would be observed in a well using desulphation. The flow cell examined the effect of temperature, supersaturation and flow rate as isolated factors in order to ensure all "combined effects" were properly controlled. From a combination of experimental data and model predictions, it was found that an increase in flow rate, temperature and supersaturation increases the rate of deposition. However, it has to be remembered that the relative amount of steady state deposition is larger at lower flow rates leading to a decrease in the observed mass of scale per litre of fluid throughput over the experiment. Hence plots using the Damköhler number to express the ratio of kinetic deposition time to residence time were developed and used to explain the results.

***Paper 2: GRAHAM, A.L., BOAK, L.S., NEVILLE, A. and SORBIE, K.S.: "How Minimum Inhibitor Concentration (MIC) and Sub-MIC Concentrations Affect Bulk Precipitation and Surface Scaling Rates", SPE Production & Operations, Vol. 21, Issue No. 1, pp.19-25, February 2006.***

This paper describes an in-depth study of both bulk precipitation and surface deposition i.e. homogenous versus heterogeneous nucleation for a barium sulphate scaling system. SI concentrations were applied both below and above MIC as obtained from conventional bulk jar tests performed at 50$^{o}$C for the SI, PPCA. These tests were performed in a similar static jar test manner. However, an additional step of using a rotating hastelloy surface was introduced in the experiment. Temperature in a production system can range from as low as 4$^{o}$C to 95$^{o}$C and above, hence a range of temperatures were studied to establish the scaling tendency of the brine at different stages of production. From the experiments, a general schematic trend was identified for both the surface and bulk efficiency trends at 5, 50, 95$^{o}$C, as shown in Figure 31.

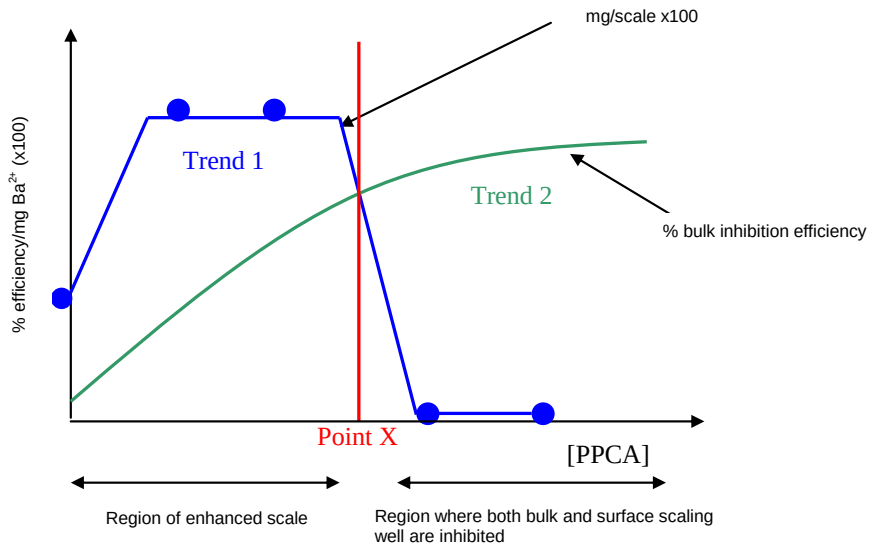



Figure 31: Schematic diagram of general surface and bulk efficiency trends

Figure 31 shows that an increase in [SI] increases the bulk inhibition efficiency performance. However, the surface studies show enhanced surface growth at a [SI] below point X, the minimum inhibitor concentration MIC, where both bulk and surface scaling should be controlled. At [SI] < MIC, the [SI] present is trying to stop the bulk scaling which means that the faster reaction of heterogeneous nucleation at the surface is not being controlled. The insufficient [SI] is unable to make a surface film to prevent the heterogeneous nucleation. At the two extreme temperatures, the data was more erratic due to the fact that conflicting kinetic and supersaturation processes were occurring. The reactions at 50$^{o}$C appeared to be more controlled by the SI. An MIC was identified for the PPCA SI being examined, at which both surface and bulk scale formation were controlled at 5, 50 and 95$^{o}$C. Other important points to highlight were that both scale inhibition efficiency and the effect of a specific SI on crystal morphology varies between surface and bulk processes. It was also found that surface scaling can actually be promoted by the addition of SI at sub-MIC levels. However, a 'map' of the sub-MIC region was built, allowing the identification of the region in which enhanced surface deposition occurred. A schematic diagram of the various zones of inhibition that can occur alongside the related kinetic effect was constructed (Figure 30 above) and summarises the various regions of surface and bulk scaling and the level of inhibition. By establishing this sub-MIC SI level and identifying that different scaling zones can exist in a brine system, a better understanding of where potential problems with sub-MIC levels occurring has been gained. This is particularly important when considering

SI re-treatment, for the protection of key components such as Electrical Submersible Pumps (ESP).

### 1.3.8 *Alternative Processes to 'Squeeze' Treatments*

Although the most common measure taken to control scale formation is the application of scale inhibitors, there are other alternative options that may be better suited for the more complicated co-mingling or deepwater well structures that are frequently being installed nowadays. Alternative processes such as sulphate removal through desulphation plants (Collins, I.R. 2004; Jordan, M.M. 2006; Simpson, C.M. 2005; Vu, V.K. 2000), produced water re-injection (Furtado, C.J.A. 2005) and water shut-off to reduce volumes of scaling brine produced (Andersson, G. 2008; Williams, G. 2006) can be applied. Alternative chemical approaches can also be carried out. Options being considered include the use of solid proppant (Jordan, M.J. 2004), micro-emulsions (Collins, I.R. 2001) or the use of non-aqueous scale inhibitor treatments (Jordan, M.M. 2006; Wat, R.S. 1999) - encapsulated in a number of different forms such as pellets or as a micro-encapsulated scale inhibitor (Bourne, H.M. 2000), to ensure that no water enters the system (Graham, G.M. 2002c). However, problems may also be encountered with these alternative techniques (Chen, P. 2004; Mackay, E.J. 2007; Bedrikovetsky, P. 2006).

Modelling approaches can be used to find the optimum scale management package for a given reservoir and such software includes various thermodynamic prediction programs (Collins, I.R. 2004; Petrotech; Mackay, E.J. 2002/2003c), reservoir fluid flow simulators (Mackay, E.J. 2003a, 2003b; Vazquez, O. 2006) and analytical models (Mackay, E.J. 2000) which can be combined to assess the risk of all these techniques. Published work has shown that by combining reservoir modelling and scale prediction software, the severity and location of scaling problems, can be identified (Chekani, M. 2004; Mackay, E.J. 2000, 2003a, 2002/2003c; Petrotech). This type of modelling is not restricted to vertical wells; horizontal wells also require life cycle management (Mackay, E.J. 1998). A major role is played by these models through identification of how different reservoirs and brine compositions react to specific conditions such as T and P. However, these calculations should be supported by laboratory studies using representative field conditions and kinetics.

One alternative to scale inhibitor protection is the desulphation process where the level of sulphate in the injected seawater brine (~2900ppm) is greatly reduced (to ~20-40ppm). This is particularly useful for reservoirs of high scaling tendency (e.g. high $Ba^{2+}$) where the placement of scale inhibitor chemicals is uncertain due to long tie-backs. This process was first introduced to the industry in 1988 by Marathon in the Brae Reservoir of the North Sea (Hardy, J.A. 1994). Normally the desulphation process uses nano-filtration membranes in a conventional single pass or two stage configurations. However, another type of sulphate removal using reverse osmosis can potentially remove sulphate ions to levels of <40mg/l, but it is very expensive (Collins, I.R. 2004). Therefore although reverse osmosis was identified as a possible solution, this project went forward with an advanced two-pass configuration of nano-filtration achieving sulphate levels of ~20mg/l with less expenditure on the sulphate reducing plant upgrade. Any desulphation process involves significant costs at the outset and needs to be considered very carefully at the CAPEX stage of field development.

In recent work (Boak, L.S. 2005), thermodynamic modelling and experimental studies were conducted for brine compositions based on Marlim Leste field conditions (Mota, R.O. 2004; Bezzera, M.C.M. 2004). Using the thermodynamic modelling, supersaturation and precipitation potentials in the system were first calculated assuming no precipitation reactions in the reservoir. Sensitivity calculations were then performed to investigate the effect of brine mixing both deep in the reservoir and at the production well. Supersaturation and precipitation levels were then re-calculated assuming in-situ stripping has reduced [$Ba^{2+}$] and/or [$SO_4^{2-}$] levels at the wellbore. These calculations have assumed that there has been no release of sulphate ions from the reservoir rock formation. However, a potential issue to address could be that an additional concentration of sulphate ions has been generated by fluid rock interactions which encourage the dissolution of the reservoir rock and hence has to be accounted for in the calculations. Static (uninhibited) $BaSO_4$ precipitation experiments were conducted to determine the limiting sulphate level that removes the requirement for squeeze treatments. A simple rate law was found and used to define 'safe operating envelopes' where the barite precipitation is sufficiently slow, negating any requirement for squeeze treatments. Some risk is associated with these safe envelopes due to uncertainties in the determination of the rate constant, k, for barium deposition. Based on further kinetic analysis, the rate at which the barite deposition may occur was established, thus identifying where the system would deposit barite slowly and where it would reach its

full equilibrium deposition limit relatively quickly. This work presents both a methodology and also some analytical modelling tools for establishing, on a sound technical basis, the answer to the question: What level of sulphate reduction is required to eliminate the need for scale inhibitor squeezing? The results from this paper were implemented by the co-authors Petrobras. Their desulphation system removes sulphate down to 50ppm and when the filter cartridges are new, down to 10ppm. The theory of slower kinetics, in conjunction with prediction packages, was used by StatoilHydro to understand their Oseberg and Brage Fields, when a lower than expected scaling regime was observed (Ramstad, K. 2009).

Further work builds on this paper (Boak, L.S. 2007a) by considering (a) the kinetics of "seeded" tests (scaling with particulates present) which would be representative of initial scaling or sand production in the oilfield system and (b) realising from these kinetic results that the scaling ion should reach equilibrium as opposed to being entirely consumed, hence allowing the model to become more representative of field conditions. Error bars were also established around the previously constructed moderate 'safe operating envelopes'.

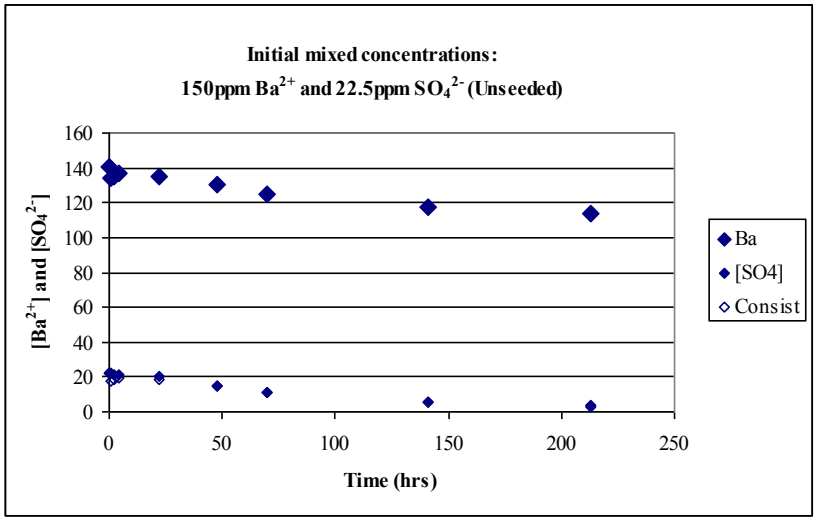
***Paper 3: BOAK, L.S. and SORBIE, K.S.: "The Kinetics of Sulphate Deposition in Seeded and Unseeded Tests", SPE Productions and Operations, Vol. 22, Issue no. 4, pp.442-450, November 2007.***

Following previous work (Boak, L.S. 2005), this paper investigated what level of sulphate ions in a low scaling sea water system can be tolerated to ensure that no scale inhibitor squeeze treatments are required, or at least they are reduced in quantity. In addition, this work also studied the effect of seeding. Un-seeded tests gave a slower kinetic growth rate, as proto-crystals have to be first formed by crystal nucleation and then they subsequently grow by homogeneous nucleation. The addition of fine powdered barite crystals to a supersaturated brine mixture accelerates barite deposition i.e. heterogeneous nucleation. This induces an immediate crystal growth mechanism that occurs on the high surface area of the seed crystals i.e. avoiding the nucleation step allows more rapid crystal growth. This seeding is representative of barite particulates which may already be in the production system or of fines which are generated from reactions with the reservoir rock and are present in the fluids. A large range of static

kinetic deposition experiments, both un-seeded and seeded, were performed over long residence times, as illustrated in Figure 32. The consistent values relate to sulphate concentrations that have been derived from the amount of barium removed from the solution, whilst the [$SO_4$] trends are ICP measured data values. Good agreement is found between the different approaches, inferring that the sulphur ICP analysis performed to calculate the [$SO_4$], is reliable.

This prediction model of working around a 'safe envelope' of desulphation and the introduction of seed particles which increase kinetic rates of reaction is very relevant to the industry due to the close representation of potential field conditions i.e. if sand fines or barite crystals are present. Careful consideration should be given to this concept.

(a)




(b)

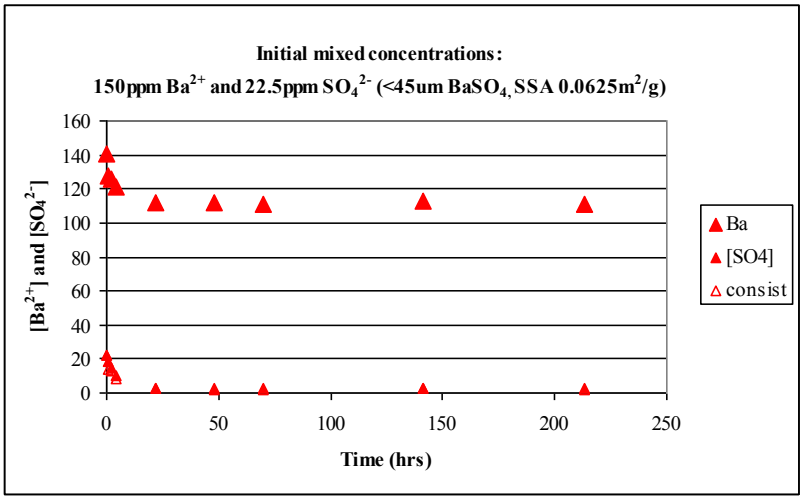



Figure 32: Plots of [$Ba^{2+}$] vs. time and [$SO_4^{2-}$] vs. time over a residence time of 213hrs for initial mixed concentrations of [$Ba^{2+}$]=150ppm (140ppm +/- 5ppm) and the normal 22.5ppm (20ppm +/- 2ppm) [$SO_4^{2-}$] level for both the measured experimental and the

consistent values of [$SO_4^{2-}$]; (a) un-seeded and (b) <45µm $BaSO_4$ seeds, with Specific Surface Area (SSA) =0.0625$m^2$/g

The outcome of these tests showed that seeded tests came to equilibrium much quicker than the un-seeded tests, more so if barite was present rather than sand and also if a higher surface area of seed crystal was present, as shown in Figure 33.

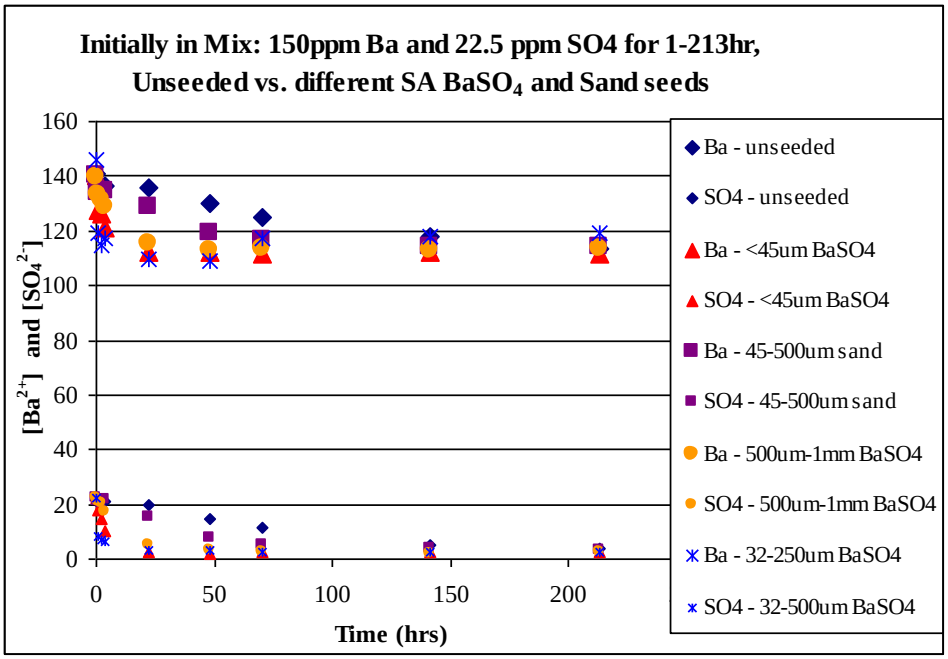



Figure 33: Plot of [$Ba^{2+}$] vs. time and [$SO_4^{2-}$] vs. time over a residence time of 213hrs for initial mixed concentrations of [$Ba^{2+}$]=150ppm (140ppm +/- 5ppm) and the normal 22.5ppm (20ppm +/- 2ppm) [$SO_4^{2-}$] level for both the measured experimental and the consistent values of [$SO_4^{2-}$]; A comparison between all the un-seeded and seeded tests

It was found that the seeded test results closely matched MultiScale predictions, especially when the model's rate law took into account the solubility product present. Over a sufficiently long time period (>50hrs -150hrs), all solutions, whether seeded or un-seeded, came to equilibrium. It was found that 1-50hr tests were not long enough to determine the final solubility accurately, therefore in the model it should be treated as a sensitivity parameter.

An analytical approach of developing better rate laws for the deposition model than those incorporated in the model (Boak, L.S. 2005) was addressed. In that previous work, the barite deposition was described by the kinetic equation below, Equation (7):

$$\left(\frac{d[Ba^{2+}]}{dt}\right) = -k.[Ba^{2+}].[SO_4^{2-}] \qquad (7)$$

This is not strictly true as barite has some solubility at high levels of sodium chloride and the above model would continue until either the barium or sulphate ion was zero instead of limiting to an equilibrium value, taking account of the solubility of barite. This equilibrium solubility was therefore an addition to the model in this paper, giving a kinetic deposition rate law of the following form, Equation (8):

$$\left(\frac{d[Ba^{2+}]}{dt}\right) = -k.\left([Ba^{2+}].[SO_4^{2-}] - K_{sp}\right) \qquad (8)$$

The definitions for the terms are given in Paper 2 and k and $K_{sp}$ can be found in the nomenclature. Although the previous paper had developed the safe working envelopes for desulphation under a relaxed, moderate and conservative regime, it has to be stressed that envelopes need to be established for specific brine mixing systems and conditions, especially temperature. In this paper, further development work investigated the error around the moderate safe envelope. This was achieved by examining +/- 20% of the sulphate concentration that lay on the safe envelope. As expected, a slightly higher $[SO_4^{2-}]$ increased the deposition rate and a slightly lower one decreased it, as shown in Figure 34.

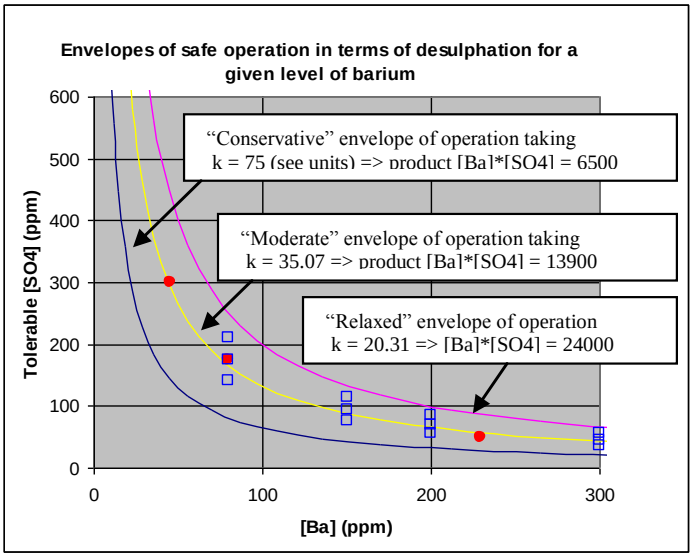



Figure 34: Envelope of tolerable levels of $[SO_4^{2-}]$ as reached by desulphation for given levels of barium concentration based on acceptable rate of barium loss from solution, R.

The “conservative” conditions are the strictest in terms of desulphation requirements. The initial experimental points (Boak, L.S. 2005) (•) are for experimental cases where very little barium deposition was observed over 22 hrs. New experimental points (□) refined the “moderate” envelope and were examined for deposition over 213 hrs

It is believed there is still a need and use for a kinetic risk model, as it can be used to illustrate kinetic effects when sulphate reduction is involved or when a natural sulphate reduction mechanism operates, using the safe envelope approach. The rate laws are of additional importance within the model, as they can be used to predict the actual masses of barite deposited.

### 1.3.9 *Scale Inhibitor Retention Mechanisms*

In scale inhibitor squeeze treatments, the two main mechanisms of scale inhibitor retention within the reservoir formation are recognised to be adsorption (Meyers, K.O. 1985; Pardue, J.E. 1991; Sorbie, K.S. 1992a, Zhang, H. 2000), precipitation (Malandrino, A. 1995; Pardue, J.E. 1991; Zhang, H. 2000) or a combination of the two (coupled adsorption/precipitation).

Adsorption is thought to occur through an electrostatic attraction or physical adsorption between the inhibitor and formation materials (Jordan, M.M. 1994; Kan, A. 1991; King, G.E. 1989; Pardue, J.E. 1991; Sorbie, K.S. 1988, 1992a; Vetter, O.J. 1973). An isotherm is said to describe this adsorption process and corresponding squeeze lifetime (Sorbie, K.S. 1991, 1992a). In an attempt to increase squeeze lifetimes beyond that attainable by adsorption, ‘precipitation’ squeezes have been trialled in the field. This treatment is based on the precipitation or phase separation of a scale inhibitor complex, normally with calcium, within the formation (Carlberg, B.L. 1983, 1987; Pardue, J.E. 1991; Yuan, M.D. 1993). The inhibitor is then slowly released back into the production stream, based on the solubility of the inhibitor/calcium complex (Browning, F.H. 1993). Formation damage is an issue with such precipitation squeezes hence, it is best to be applied in high volume, thick zoned wells (Carlberg, B.L. 1983, 1987). Temperature is a controlling factor for this precipitation process, hence an optimum volume of pre-flush to keep the near well bore area cool is important, as it allows the main treatment to be placed further out in the formation before precipitating at high temperature, thus avoiding any near well bore formation damage (Malandrino, A. 1995; Olson, J.B. 1992). In fact, both of these mechanisms are sensitive to a number of conditions such as

pH, divalent cation concentrations (calcium or magnesium) and temperature etc. (Sorbie, K.S. 1988, Zhang, H. 2000).

In the literature, these mechanisms have been investigated by various modelling approaches (Gdanski, R.D. 2001; Sorbie, K.S. 1992a, 2005; Shen, D. 2008; Tomson, M. B. 2008) and it has been shown that there are similarities and differences with advantages and disadvantages of each. Each approach has re-evaluated equations proposed to model SI transport through porous media by (a) the mathematical structure of various equations are used to describe transport and (b) using surface chemistry assumptions and models to describe SI/rock retention. Previously a 'rule of thumb' empirical approach had been used for core flood design (Sorbie, K.S. 1991, 1992a) but over the years an engineering design approach involving laboratory core flood data and modelling has been adopted, called the Field Squeeze Strategy (Sorbie, K.S. 1994). In all of these types of studies, it was found that a good 'squeeze' treatment requires the scale inhibitor to return at a low concentration (at [SI] > MIC) for a long time period and this is governed by the inhibitor/rock adsorption isotherm used in the calculations. A 'good' adsorption isotherm shows a very steep rise in adsorption at low, near threshold, concentrations followed by a flattening of adsorption at higher concentrations (Patroni Zavala, J.A. 2008; Sorbie, K.S 1992a, 1994). Larger molecular species may give longer desorption tails but there is probably a maximum molecular size for (polymeric) SI's or irreversible adsorption may occur (Sorbie, K.S. 1992a, 1994). An alternative may be to apply a blend containing both low to medium molecular weight SI species where propagation back to the well occurs at different velocities with the smaller molecular weights appearing initially followed later on by the higher molecular weight species, resulting in a long tail profile. Hence, if the key mechanisms of this process are known, then the prediction model for squeeze treatments can be improved. One such procedure to achieve this has been through the use of static bottle tests (Kahrwad, M. 2009). To investigate if it is adsorption or coupled adsorption/precipitation that is occurring, experiments were performed using a range of different clay minerals, DETPMP scale inhibitor concentrations and pH4 and 6 conditions. The advantages of combining theory and experimental data means that the model can be enhanced, allowing better prediction/matches to field data using the Squeeze software (Patroni Zavala, J.A. 2008).

***Paper 4: KAHRWAD, M., SORBIE, K.S. and BOAK, L.S.: "Coupled Adsorption/Precipitation of Scale Inhibitors: Experimental Results and Modelling", SPE Production and Operations, Vol. 24, Issue No. 3, pp.481-491, August 2009 (Online 30th July 2009).***

This paper set out to identify the conditions where a given retention mechanism (e.g. pure adsorption or coupled adsorption/precipitation) was operating. This required us to carry out a carefully designed set of laboratory experiments under field relevant conditions. For instance, experiments were performed where the system was known to work through only one mechanism at a time. The mineral types examined were sand, chlorite, siderite, muscovite, kaolinite and feldspar at two different pH values (pH 4 & 6) and temperatures (25 & 95$^{o}$C) for a variety of different weights of substrate (10, 20 & 30g) and [DETPMP SI]'s. Parallel precipitation (or compatibility) experiments were performed in the absence of minerals in order to measure the solubility of sparingly soluble $Ca^{2+}/Mg^{2+}$/SI salts described by an equilibrium solubility product, $K_{sp}$. SEM and EDX techniques were used to analyse the $Ca^{2+}/Mg^{2+}$ - DETPMP precipitated complex. A theory was developed that describes the coupled adsorption/precipitation process as apparent adsorption versus [SI] depending on the mass/volume ratio, as denoted below, Equation (9) (refer to Paper 4 for explanation of symbols),

$$F(c_{1f}) = c_{1f} + \left(\frac{m}{V.M_{SI}1000}\right).\Gamma\left(c_{1f}\right) + \left(\frac{1}{n}\right)\left(c_{20} - \left(\frac{K_{sp}}{c_{1f}}\right)^{1/n}\right) - c_{10} \qquad (9)$$

For pure adsorption (no precipitation), the above equation predicts that all results collapse onto a single curve, the adsorption isotherm, as illustrated in Figure 35. However, if coupled adsorption/precipitation is occurring, then the "apparent adsorption" isotherm becomes a function of the ratio of mineral mass to volume of SI used (m/V).

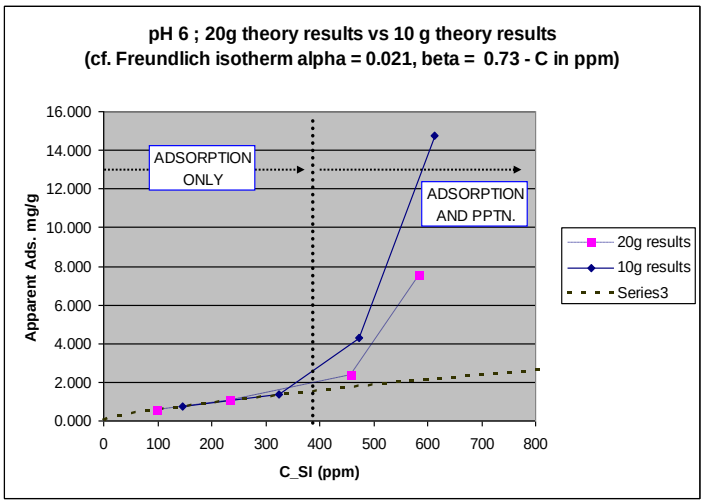



Figure 35: Calculated "apparent adsorption", Γapp vs. concentration of SI for the model parameters. Series 3 represents the ideal adsorption isotherm trend.

The model can be used for experimental predictions. The coupled adsorption/precipitation model was found to be in good agreement with the experiments.

A summary of the results highlighted that at pH4 and T=95$^{o}$C, only pure adsorption was observed for all the mineral separates studied. At pH6 and T=95$^{o}$C, coupled adsorption/precipitation was observed for all the mineral separates studied. Figure 36 only shows the siderite result. The experimental results showed a clear dependence of apparent adsorption versus [SI] on the (m/V) ratio. This behaviour was expected since the SW itself phase separates at these conditions, pH6 and 95$^{o}$C.

In all cases, a significant reduction in [$Ca^{2+}$] and [$Mg^{2+}$] was observed with increasing [SI] which at pH6 is greater than at pH4 as shown in Figure 37 and Figure 38 for siderite only. This $M^{2+}$ reduction in solution is associated with the precipitation of a $M^{2+}$-DETPMP complex. This complex was analysed by SEM-EDX and clearly gives $Ca^{2+}$, $Mg^{2+}$ and P peaks in the EDX signal.

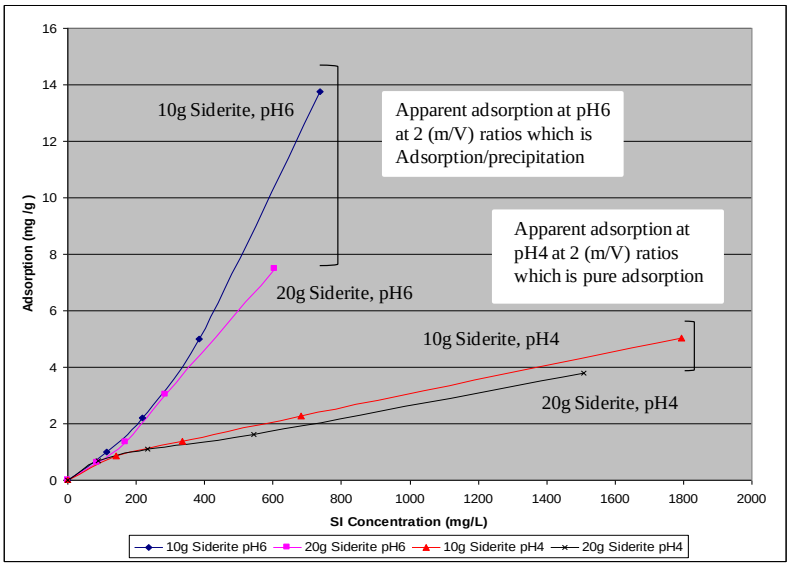



Figure 36: Apparent adsorption on siderite at pH4 and pH6 at 95°C, at various (m/V) ratios

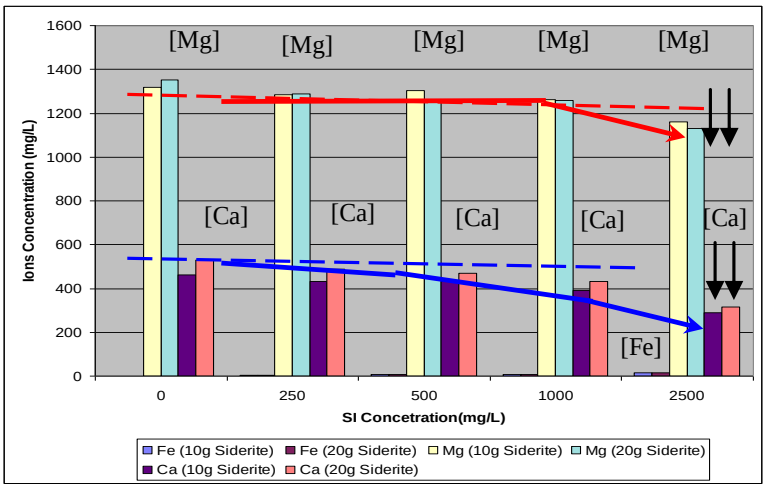



Figure 37: Fe, $Ca^{2+}$ and $Mg^{2+}$ concentration change vs. SI concentration at pH6 and 95°C (siderite)

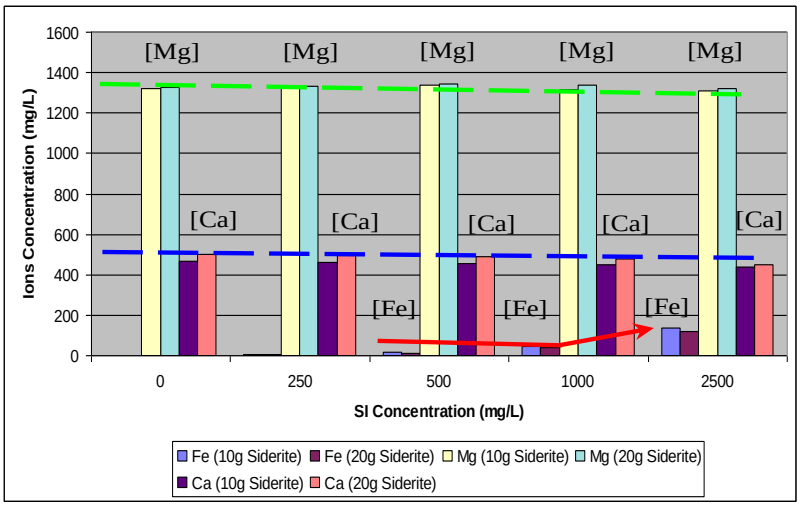



Figure 38: Fe, $Ca^{2+}$ and $Mg^{2+}$ concentration change vs. SI concentration at pH4 and 95°C (siderite)

The field significance of these findings is very high. For instance, squeeze treatments are based on design models which are a mathematical description of the SI retention mechanism involved in that application (adsorption or precipitation). This paper therefore confirmed for the first time, through theory and experimental work, how to precisely diagnose and quantify (a) pure adsorption mechanism of SI onto the rock or (b) coupled adsorption/precipitation retention. The theory was derived and the resulting equations were solved numerically to predict the experimental data which were observed to be in excellent agreement with the theory. These results can then be taken from the lab and adapted for a field situation by the adsorption/precipitation model being incorporated into a SI design tool such as SQUEEZE (Zhang, H.R. 1997). This task has now been completed by FAST at Heriot-Watt University who originally developed the model (Ibrahim, J. 2012a, 2012b; Sorbie, K.S. 2010; Vazquez, O. 2010). In practice, the use of this modified model should now allow field personnel to gain a better physical description of their squeeze treatments. Therefore the outcome of the model in the field is that improved squeeze designs give more 'fit for purpose' SI squeeze treatments (Patroni Zavala, J.A. 2008). This in turn means that a better description of the adsorption/precipitation coupled process should lead to more accurate future predictions of SI returns and better optimised treatments.

### 1.3.10 *Monitoring of Scale Inhibitor Concentrations*

After a squeeze treatment, the produced brine must be monitored at low threshold concentrations, 5ppm or less, to determine the scale inhibitor concentrations so that the timing for a re-squeeze can be correctly identified. In addition, the monitoring and collating of these low scale inhibitor concentrations allows modelling of the scale inhibitor return profile from which predictions of the future squeeze lifetimes can be obtained. The optimisation of these squeeze lifetimes can significantly reduce financial expenditure in terms of both chemical cost and deferred oil production.

Early work on scale inhibitor assay has been reported previously and detailed references are given in Boak, L.S. 2010. This work examined many problems associated with scale inhibitor analysis in both synthetic brines and in field produced waters; increasing backgrounds, interferences with the analytical procedure by other constituents within the produced brines, precipitation, particle drop out and also limitations of the analytical techniques. However, despite these difficulties, a number of successful procedures were

obtained for the analysis of many generically different scale inhibitors. A range of techniques were established, from wet chemical to the use of ICP, as no one technique can be used for all the generically different scale inhibitor species. The detailed techniques developed previously for oilfield SI application along with the structures of most common scale inhibitors can be found in the FAST Laboratory Manual, (Sorbie, K.S. 2006). Since these early years, these techniques have not only been widely used throughout the oil industry, but they have also been adapted and developed to allow more accurate results for the conventional scale inhibitors of that time.

However more than 15 years on, the oil industry is much more environmentally aware and one of the consequences is that more environmentally friendly scale inhibitors have been developed and applied. These are known as 'Green Scale Inhibitors' (GSI), and they do not pollute the waters around platforms and the pipeline systems through bioaccumulation and non-degradation (Inches, C.E. 2006). These GSIs are also being applied in chemical squeeze treatments. Although more environmentally friendly, they bring their own set of problems to the analysis world, such as being non-phosphorus containing, making analysis by ICP non applicable. In some cases, it may be possible that a P-tag can be attached to the GSI which for now appears to be in limited concentration making low level SI analysis by ICP potentially possible but extremely difficult. Therefore, the industry may have to resort to wet chemical techniques or other instrumentation such as HPLC (Dionex). In either case, major improvements are needed to allow low level SI assay, at <0.5ppm active in some cases, in produced brine to be achieved.

***Paper 5: Boak, L.S. and Sorbie, K.S.: "New Developments in the Analysis of Scale Inhibitors", SPE Production and Operations, Vol. 25, Issue No. 4, pp.533-544, November 2010.***

This paper describes a range of analytical approaches which have recently allowed improved chemical SI assay for wet chemical techniques, when ICP is not viable (such as for new green products with no ICP label present). In addition to the accuracy of these methods, any time saving improvements to wet chemical techniques are extremely beneficial. Table 4 details the brine compositions used in these studies.

| Ion | NSSW | Forties 'type' FW (Original [$Ca^{2+}$] = 5038ppm) | Heron 'test' FW |
|---|---|---|---|
| | ppm | ppm | ppm |
| Na | 10,890 | 31,275 | 75,000 |
| Ca | 428 | 2,000 | 42,000 |
| Mg | 1,368 | 739 | 1,930 |
| K | 460 | 654 | 11,400 |
| Ba | 0 | 269 | 1,360 |
| Sr | 0 | 771 | 1,340 |
| $SO_4$ | 2,960 | 0 | 0 |
| Cl | 19,773 | 55,279 | 207,712 |

Table 4: The brine compositions used in these analytical studies

Previously, the sulphonated copolymer (VS-Co) assay required laborious and extensive dialysis and sample preparation. However, by using amino-propyl cartridges ($NH_2$) and the Hyamine method, similar accuracy to the well established C18-Cartridge/Hyamine technique for polyelectrolytes with carboxylic functional groups was achieved as shown in Figure 39, Table 5 and Figure 40, Table 6.

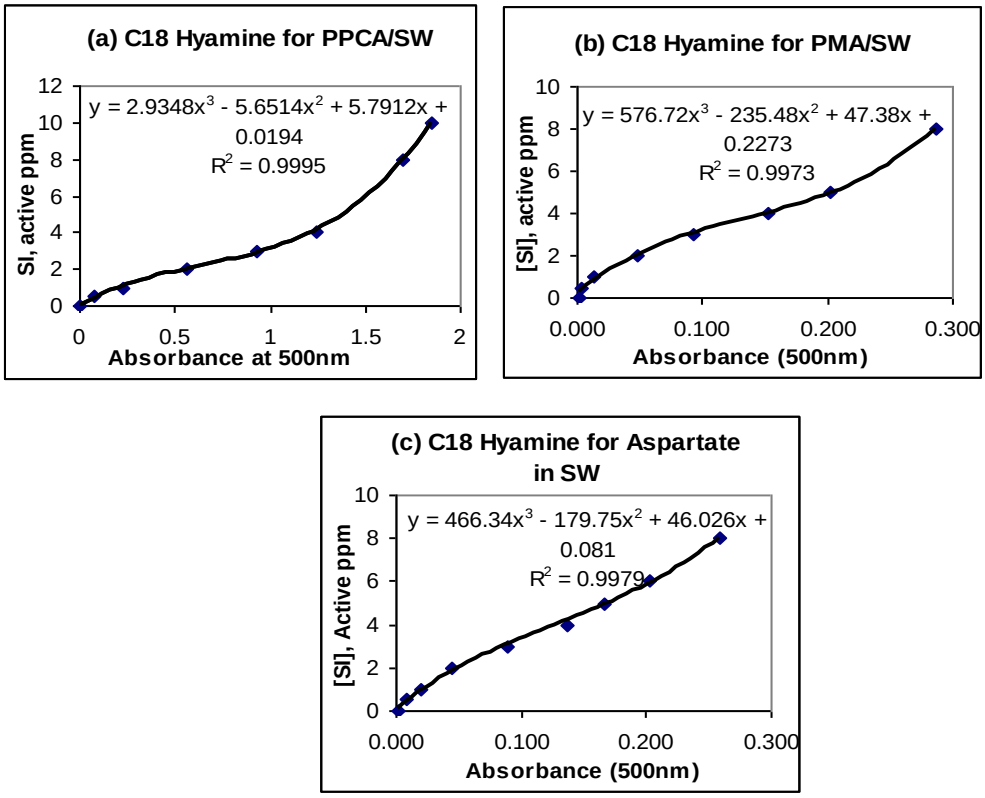



Figure 39: Examples of calibration graphs that can be obtained following the C18 Hyamine procedure for (a) PPCA, (b) PMA and (c) polyaspartate

| A SUMMARY OF THE $R^2$ COEFFICIENTS AND STANDARD REPEATS FOR PPCA, PMA, AND POLYASPARTATE USING C18 HYAMINE | | | |
|---|---|---|---|
| | Poly-Phosphino Carboxylic Acid (PPCA) | Poly Maleic Acid (PMA) | Poly Aspartate |
| Calibration $R^2$ | 0.9995 | 0.9973 | 0.9979 |
| Repeats | | | |
| 0ppm | 0.409 | –0.081 | 0.227 |
| 1ppm | | 1.04 | 1.01 |
| 2ppm | | | |
| 4ppm | | 4.15 | 4.06 |
| 5ppm | 4.76 | | |
| Note: The absorbance for the 0ppm repeat was similar to the absorbance of the 0ppm in the calibration however depending on the curve fit the determined 0ppm concentration could be higher/lower than expected. | | | |

Table 5: A summary of the $R^2$ coefficients and standard repeats for PPCA, PMA and Polyaspartate using C18 Hyamine

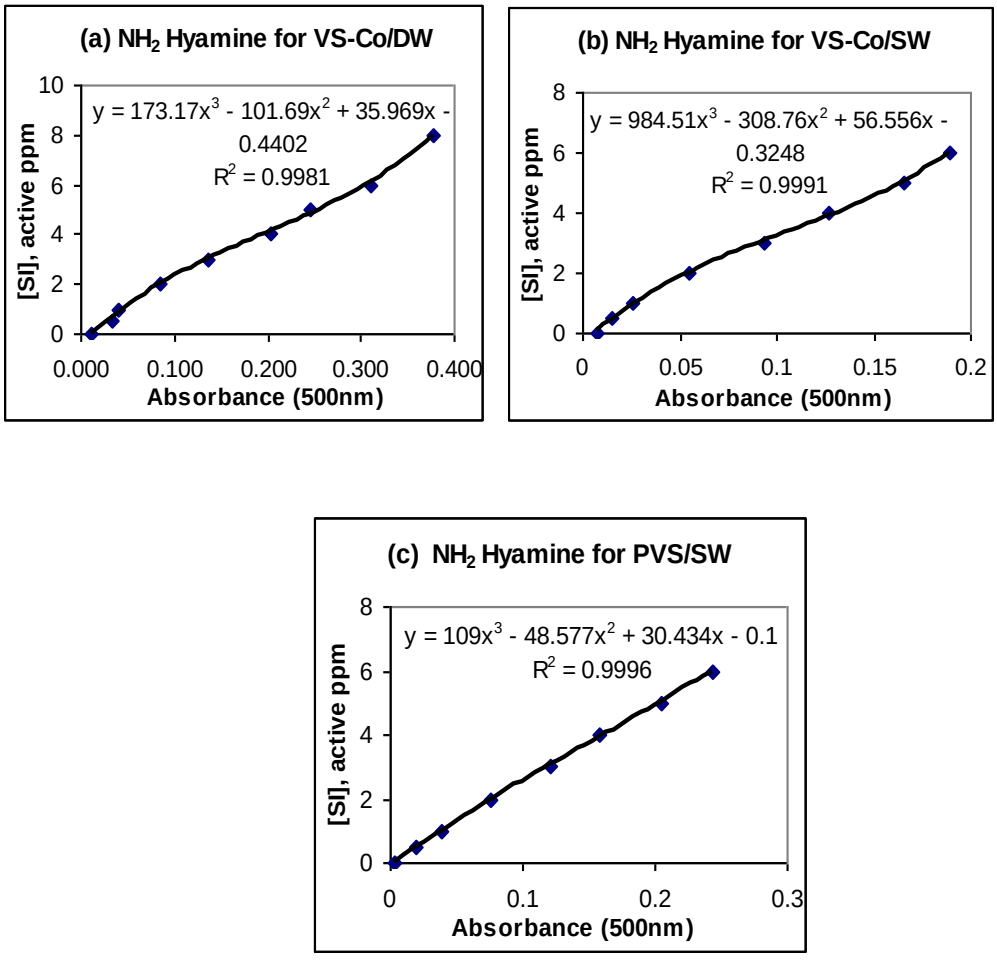



Figure 40: Calibration graphs obtained following the $NH_2$ Hyamine procedure for (a) VS-Co in DW (b) VS-Co in SW and (c) PVS in SW

| A SUMMARY OF THE $R^2$ COEFFICIENTS AND STANDARD REPEATS FOR VS-Co in DW/SW and PVS/SW USING $NH_2$ HYAMINE | | | |
|---|---|---|---|
| | VS-Co/DW | VS-Co/SW | PVS/SW |
| Calibration $R^2$ | 0.9981 | 0.9991 | 0.9996 |
| Repeats | | | |
| 0ppm | –0.159 | –0.103 | 0.081 |
| 1ppm | 0.804 | 0.897 | 0.965 |
| 3ppm | | | 3.04 |
| 4ppm | 4.02 | 3.81 | |
| 5ppm | | | 4.94 |
| 6ppm | 5.98 | | |
| Note: The absorbance for the 0ppm repeat was similar to the absorbance of the 0ppm in the calibration however depending on the curve fit the determined 0ppm concentration could be higher/lower than expected. | | | |

Table 6: A summary of the $R^2$ coefficients and standard repeats for VS-Co in DW/SW and PVS/SW using $NH_2$ Hyamine

This has been achieved due to the different bonding regimes between the two different types of cartridge: For C18 - SI is applied at pH2, the SI is fully protonated and the SI is retained on the C18 through H-bonding/weak interactions whilst the salts flow through. However, for the $NH_2$ cartridge which is a more polar and basic cartridge, a sulphonated SI at pH2 is dissociated due to low pKa value so strong ionic bonds form with the cartridge and the salts flow through. A stronger eluent of 0.1N NaOH was required, compared with the 5% sodium citrate, to release the SI from the cartridge due to the strong ionic bonding formed.

The Oasis® 2x4 method, which is extensively used in the pharmaceutical industry, has been applied to oilfield SI analysis. In principle, this method is able to assay all types of polymeric scale inhibitors – both conventional and green SI. The calibration and repeat results shown in Figure 41 and Table 7 show assay results for the VS-Co SI in a wide variety of different brine salinities from distilled water (DW) to high salinity formation water e.g. Heron type FW. Better accuracy was achieved for low end values on a 0-2ppm calibration. There is a significant decrease in the absorbance signals recorded with increasing salinity which did not improve with a higher capacity sorbent cartridge.

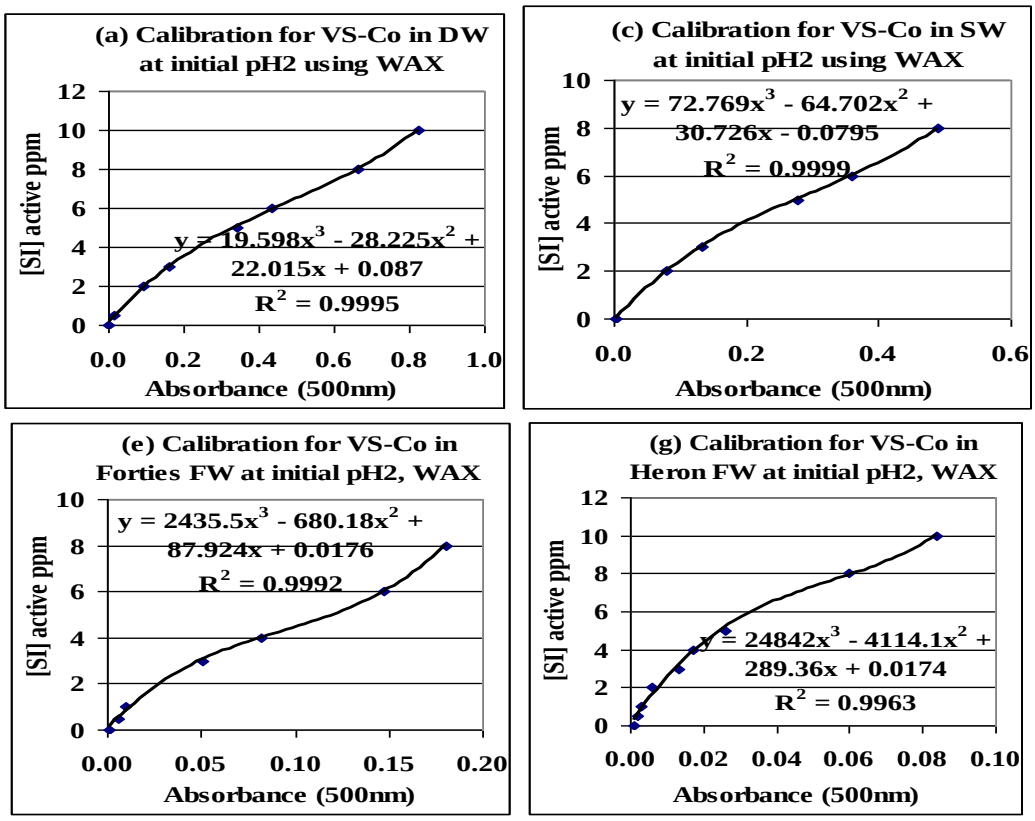



Figure 41: Calibration graphs obtained for VS-Co initially in various salinity brines: DW, NSSW, Forties FW and Heron FW; (a, c, e, g) Full 0-8 or 0-10ppm active range achieved

| EXAMPLE OF THE $R^2$ COEFFICIENT AND STANDARD REPEATS FOR THE 10-mL ANALYSIS OF THE SIs, VS-Co IN THE VARIOUS SALINITY BRINES: DW, NSSW, FORTIES FW, AND HERON FW; (a) FULL CALIBRATION REPEATS, (b) 0–2ppm CALIBRATION REPEATS | | | | |
|---|---|---|---|---|
| (a) Full Calibration | DW | NSSW | Forties FW | Heron FW |
| Calibration $R^2$ | 0.9995 | 0.9999 | 0.9992 | 0.9963 |
| Repeats | | | | |
| 0ppm | 0.109 | –0.049 | 0.105 | 0.303 |
| 0.5ppm | 0.336 | 0.147 | 0.400 | 0.303 |
| 1ppm | 0.661 | 0.538 | 0.906 | 0.849 |
| 4ppm | 3.15 | 3.92 | 4.02 | 4.20 |
| 6ppm | 5.77 | 5.90 | 5.17 | 5.85 |
| (b) 0–2 Calibration | DW | NSSW | Forties FW | Heron FW |
| Calibration $R^2$ | 1.0000 | 0.9989 | 0.9972 | 0.9997 |
| Repeats | | | | |
| 0ppm | 0.109 | –0.098 | –0.024 | –0.008 |
| 0.5ppm | 0.357 | 0.274 | 0.397 | –0.008 |
| 1ppm | 0.823 | 0.934 | 1.049 | 0.986 |
| Note: The absorbance for the 0ppm repeat was similar to the absorbance of the 0ppm in the calibration however depending on the curve fit the determined 0ppm concentration could be higher/lower than expected. | | | | |

Table 7: Example of the $R^2$ coefficients and standard repeats for the 10ml analysis of the SIs, VS-Co in the various salinity brines: DW, NSSW, Forties FW and Heron FW; (a) Full calibration repeats, (b) 0-2ppm calibration repeats

ICP analysis is normally performed for various elements, such as P, Ca, Mg, Fe etc., in aqueous solutions. However, in this work various elements have also been assayed in

the oil phase using ICP, where calibrations and repeats within 5-10% error were achieved, Table 8.

| ACCURACY AND REPEATABILITY FOR SEVERAL IONS DURING ICP OIL ANALYSIS IN WHITE SPIRIT | | | | | | | |
|---|---|---|---|---|---|---|---|
| | 317.933nm | | | | 213.618nm | | |
| Sample Name | Ca | Corrected Ca | Mean | Sample Name | P | Corrected P | Mean |
| 0ppm | 0.002 | 0.002 | 0.001 | 0ppm | 0.000 | 0.00 | 0.00 |
| 0ppm | 0.000 | 0.000 | | 0ppm | 0.000 | 0.00 | |
| 5ppm | 4.93 | 4.97 | 4.96 | 5ppm | 5.14 | 5.02 | 5.00 |
| 5ppm | 4.91 | 4.95 | | 5ppm | 5.10 | 4.98 | |
| 10ppm | 9.67 | 9.84 | 9.90 | 10ppm | 10.01 | 9.79 | 9.82 |
| 10ppm | 9.78 | 9.96 | | 10ppm | 10.06 | 9.84 | |
| | 259.940nm | | | | 181.978nm | | |
| Sample Name | Fe | Corrected Fe | Mean | Sample Name | S | Corrected S | Mean |
| 0ppm | 0.000 | 0.000 | 0.000 | 0ppm | –0.120 | 0.012 | 0.001 |
| 0ppm | 0.000 | 0.000 | | 0ppm | –0.145 | –0.010 | |
| 5ppm | 5.02 | 4.97 | 4.97 | 5ppm | 5.52 | 4.99 | 4.66 |
| 5ppm | 5.03 | 4.98 | | 5ppm | 4.79 | 4.34 | |
| 10ppm | 9.95 | 9.84 | 9.86 | 10ppm | 9.75 | 10.03 | 10.08 |
| 10ppm | 10.00 | 9.89 | | 10ppm | 9.84 | 10.12 | |
| | 279.553nm | | | | 371.029nm | | |
| Sample Name | Mg | Corrected Mg | Mean | Sample Name | Y | Corrected Y | Mean |
| 0ppm | 0.000 | 0.000 | 0.000 | 0ppm | 0.001 | 0.000 | 0.000 |
| 0ppm | 0.000 | 0.000 | | 0ppm | 0.001 | 0.000 | |
| 5ppm | 5.05 | 5.07 | 5.06 | 5ppm | 4.97 | 5.03 | 5.05 |
| 5ppm | 5.03 | 5.05 | | 5ppm | 5.02 | 5.08 | |
| 10ppm | 9.85 | 9.98 | 10.02 | 10ppm | 10.00 | 10.15 | 10.16 |
| 10ppm | 9.92 | 10.05 | | 10ppm | 10.03 | 10.18 | |
| | 178.229nm | | | | 670.784nm | | |
| Sample Name | P | Corrected P | Mean | Sample Name | Li | Corrected Li | Mean |
| 0ppm | –0.011 | 0.011 | 0.014 | 0ppm | 0.008 | –0.020 | –0.020 |
| 0ppm | –0.004 | 0.018 | | 0ppm | 0.007 | –0.021 | |
| 5ppm | 4.88 | 5.00 | 4.97 | 5ppm | 5.26 | 4.94 | 4.99 |
| 5ppm | 4.82 | 4.94 | | 5ppm | 4.37 | 5.04 | |
| 10ppm | 9.72 | 9.51 | 9.47 | 10ppm | 11.53 | 10.71 | 10.84 |
| 10ppm | 9.63 | 9.42 | | 10ppm | 10.94 | 10.97 | |

Table 8: A table showing the accuracy and repeatability for several ions during ICP oil analysis in white spirit

After solving some compatibility issues (phase separation), the concentration of an oil-tolerant SI was determined successfully over a range of 0-10 and 0-2500ppm active SI. The 0-10ppm active results for different SI:white spirit ratio mixes show good agreement with the known concentrations, as shown in Table 9.

| DATA RECORDED FOR STANDARD REPEATS DURING THE 0–10ppm ACTIVE SI IN 10% EGMBE/SI: 90% WHITE SPIRIT AND 50% EGMBE/SI: 50% WHITE SPIRIT MATRIX RATIOS* | | | | | |
|---|---|---|---|---|---|
| 10% E : 90% WS | 178.229nm | | 50% E : 50% WS | 178.229nm | |
| Sample Name | P | Corrected P | Sample Name | P | Corrected P |
| 0ppm | 0.036 | 0.000 | 0ppm | –0.053 | –0.038 |
| 0.5ppm | 0.459 | 0.490 | 0.5ppm | 0.375 | 0.508 |
| 1ppm | 1.007 | 0.999 | 1ppm | 0.941 | 1.05 |
| 2.5ppm | 2.33 | 2.51 | 2.5ppm | 2.37 | 2.48 |
| 5ppm | 4.96 | 4.96 | 5ppm | 4.69 | 4.87 |
| 10ppm | 9.91 | 9.97 | 10ppm | 9.78 | 9.93 |
| * The first column contains the Raw ICP Data and the second the Drift Corrected Data. | | | | | |

Table 9: Data recorded for standard repeats during the 0-10ppm active SI in 10% EGMBE/SI: 90% white spirit and 50% EGMBE/SI: 50% white spirit matrix ratios. The 1st column contains the raw ICP data and the 2nd the drift corrected data

A background matrix–matching Hyamine technique has been developed which allows any chloride ion effects on the chelating process between the Hyamine and SI to be negated, allowing accurate analysis of low polymeric SI concentrations. This is achieved by matrix matching the background fluid for the sample and calibration standards; for example, by using the same dilution factor from a SW background to a DW background for both, hence giving equivalent chloride ion concentration/interferences in both. This process was successfully performed for x10, 5, 2.5 and 2 dilution factors for the matrix matching technique from SW to DW as shown in Figure 42. For instance, if a sample gave an absorbance value of ~0.24 then depending on which calibration had been used during the analysis, the determined ppm value of the sample could range between ~2.7 – 6ppm active SI. Therefore it is very important to matrix-match the background of the sample and calibration. With no dilutions at all in DW i.e. at full SW chloride ion composition, ~19700ppm, a calibration cannot be achieved.

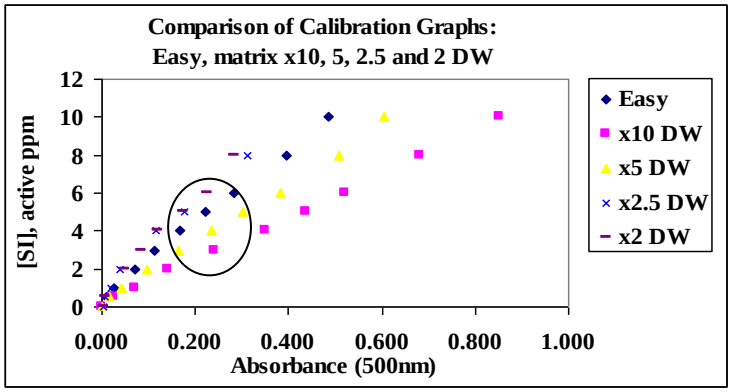



Figure 42: Comparison of all calibration types – Easy Hyamine and Matrix matched Hyamine at x10, 5, 2.5 and 2 DW dilutions

ICP (analysing for phosphorous P content) and wet chemical techniques have been able to detect a 'yellow' P-tagged co-polymer type SI and the results from each method show excellent correlation. The ability to apply two independent analytical methods to a given species offers important advantages when more than one SI is deployed in a field system. Two ICP methods were employed; the PHOS method (Peak height) and the P POLYMER method (Peak area - Gaussian). Each method had two spectral lines; 177.440 and 214.914nm wavelengths. Within each method, the 177.440nm line examined the low end calibration standards, 0, 5, 50ppm and the 214.914nm line, the high end, 0, 50, 500, 2500ppm active in North Sea Seawater (NSSW). The results observed showed that all the species examined could be detected by ICP including the P-tagged co-polymer, over the range 0-2500ppm. The ICP process was repeated for a low end calibration of 0, 5, 10ppm active to compare the level of quantification (LOQ) between the P-tagged co-polymer and the PPCA. The results in Table 10 highlight that the detection of the P-tagged co-polymer is very similar to the PPCA by ICP at these low concentrations with an LOQ of 0.5ppm active although lower concentrations could be achievable. The signal intensities for both methods indicated that the P-tagged co-polymer contains more P content within its structure than PPCA. This greater P signal would be advantageous for its detection at lower concentrations or in more severe brine systems, especially if wet chemical techniques are required for its analysis.

| **RESULTS FOR LOW-END CALIBRATIONS, 0–10ppm ACTIVE, FOR THE SIs P-TAGGED COPOLYMER AND PPCA** | | | | | | |
|---|---|---|---|---|---|---|
| | PHOS Method (peak height) | | | | | |
| Determined Concentrations for | Known Active Concentrations | | | | | |
| 177.440nm line | 0 | 0.5 | 1 | 2.5 | 5 | 10 |
| P tagged co-polymer | –0.035 | 0.472 | 1.00 | 2.38 | 5.04 | 10.53 |
| PPCA | –0.021 | 0.489 | 0.929 | 2.63 | 4.84 | 10.51 |
| | P Polymer Method (Gaussian peak area) | | | | | |
| Determined Concentrations for | Known Active Concentrations | | | | | |
| 177.440nm low line | 0 | 0.5 | 1 | 2.5 | 5 | 10 |
| P tagged co-polymer | 0.017 | 0.488 | 0.957 | 2.40 | 4.91 | 10.15 |
| PPCA | 0.005 | 0.519 | 1.002 | 2.44 | 4.90 | 9.85 |
| 177.440nm high line | 0 | 0.5 | 1 | 2.5 | 5 | 10 |
| P tagged co-polymer | –0.035 | 0.482 | 1.02 | 2.46 | 4.90 | 10.10 |

Table 10: Results for low end calibrations, 0-10ppm active, for the SIs P-tagged copolymer and PPCA

In addition to ICP, a number of wet chemical techniques were investigated to see if they could not only detect the P-tagged Co-polymer but, by using the same standard solutions, could they determine corresponding values for these chemical techniques by

each wet chemical technique. Additional independent 1000 and 5000ppm active solutions were also analysed as illustrated in Table 11. There are variations in the recorded concentrations of the ICP solutions but they are of the correct magnitude except for 50 and 500ppm by Easy Hyamine – due to matrix matching effects, discussed above.

| SUMMARY TABLE FOR THE DETERMINED CONCENTRATIONS OF THE P-TAGGED COPOLYMER ICP STANDARDS BY WET-CHEMICAL ANALYSIS | | | |
|---|---|---|---|
| | Known Active Concentrations For | | |
| P Tagged Co-polymer | Amino Propyl Cartridge/Hyamine | Oasis - WAX/Hyamine | Easy Hyamine |
| 0 | 0.244 | 0.205 | 0.466 |
| 5 | – | – | – |
| 50 | 53.56 | 52.49 | 109.94 |
| 500 | 510.22 | 502.81 | 597.85 |
| 1000 | 1023.7 | 981.73 | 1149.04 |
| 2500 | 2635.6 | 2394.31 | 2565.72 |
| 5000 | 5181.63 | 4770.08 | 5405.46 |

Table 11: Summary table for the determined concentrations of the p-tagged Co-polymer ICP standards by wet-chemical analysis

The wet chemical analysis for the P-tagged co-polymer was then compared with the corresponding ICP determined values, (Figure 43) which shows that the PHOS ICP methods are a slightly better match (shown by linear relationships) with the wet chemical analysis, whilst the Oasis technique appears low at 2500 and 5000ppm$_{act}$ SI.

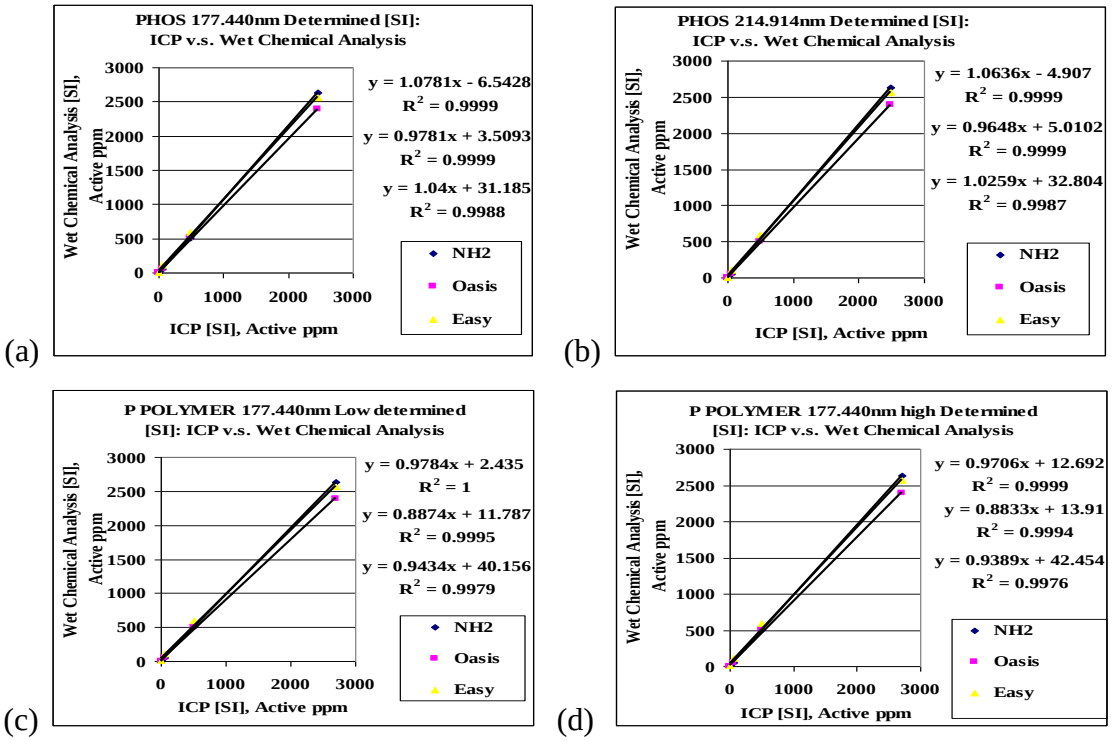



Figure 43: A Comparison of the ICP Determined [SI] with the Wet Chemical Determination for the P-Tagged Co-polymer in NSSW, (a) PHOS 177.440nm, (b) PHOS 214.914nm, (c) P POLYMER 177.440nm low and (d) P POLYMER 177.440nm high

This analytical paper has improved or indeed, advanced wet chemical techniques for scale inhibitor analysis from the returning treatments, allowing some scale inhibitor chemicals to be detected using less laborious procedures. This [SI] monitoring allows the timing for a re-squeeze to be determined. In addition, the greater P content found for the P-Tagged Co-polymer would be useful under field conditions or in a harsher brine system than NSSW where interferences could be present in the produced water making analysis of the SI more difficult i.e. it would be easier to identify the SI content from the background response. From the paper, it has been shown there are a number of comparable techniques available to detect this P-Tagged Co-polymer SI offering greater flexibility to the analyst. In addition, measurements can be performed by different techniques and the results compared to ensure that each analysis is consistent, if difficulties are experienced. There may also be potential for deploying such species with other P-containing phosphonates in subsea wells for example; a combination of total P and polymer wet chemical detection may allow the assay of 2 species to be performed.

### 1.4 Field Significance

The squeezing of scale inhibitor species is the most commonly used technique to control reservoir scale formation so tests are required to assess the performance of SI's against scale formation when conditions are varied. This increased knowledge on SI mechanisms helps all sectors to select or manufacture the appropriate chemical for field conditions. We have achieved this using specific experiments and predictions to optimise models which make operator field treatments more cost effective, for a longer return. This is aided by improved/advanced wet chemical techniques for SI. The results arising from this thesis have the following detailed field significances:

**Improved understanding of the fundamental mechanisms;**

- If functional groups for a specific set of conditions is known SI could be selected more easily without such extensive screening prior to final evaluation and deployment
- Improved SI products could be manufactured specifically for known conditions;
    - Levels of $Ca^{2+}$/$Mg^{2+}$ change, Type 1/2 or A/B
        - » Potential Type 2 for high $Ca^{2+}$ field avoiding Type B

    - » Potential Type 1 for low $Ca^{2+}$ or $Mg^{2+}$ present as less affected by cations than Type 2
  - Consider scaling tendency, reservoir T, $[Ca^{2+}]$, $[Mg^{2+}]$, pH
    - » During a field's production life
    - » Compromise between environmental/reservoir influences & SI performance

**Using kinetic models and [SI] monitoring for better protection of specific equipment or system areas; ESP, valves**

- Identification of re-squeeze timing; remembering that the surface MIC could be greater than the bulk MIC
- Avoids increased surface growth/deposition rates due to < MIC [SI]'s and the swap out of equipment from difficult locations

⇨ Costs of remedial work reduced and optimised models give better predictions from squeeze calculations

**'Safe envelope approach'; Suggests $[Ba^{2+}]$ and $[SO_4^{2-}]$ for no squeeze or reduced treatment requirement**

- Observe $[SO_4^{2-}]$ reductions; mechanical or natural stripping affect scaling regime
- Rate law inclusion allows prediction of actual barite masses deposited
- Calculations adapted for a predictive STR model (Boak, L.S. 2007b) which has been applied in a field situation where possible barite deposition was being observed in gravel packs (Shields, R.S. 2010)

**Using a new retention model allows better predictions/matches of field data using squeeze software**

- Making field treatments more cost effective
- Achieved a longer optimised SI return profile using additional retention information
- Squeeze software predictions; Enhanced by improved analysis for the returning SI when inputted into model as data

**Improved detection aids for scale inhibitor analysis**

- Less time consuming wet chemical techniques
- Found no. of techniques to detect new p-tagged co-polymer – flexibility
- If species with other P-containing phosphonates; multiple detection methods available for it, in conjunction with full P content

## 1.5 Conclusions

The work that this thesis is based on has highlighted a number of important findings which help the oil industry to understand how different scaling processes are connected, and how either the process or the chemicals applied in a given situation can be influenced by changes in environmental conditions or other factors. The detailed conclusions of this work are as follows:

1. From these studies it has been shown that a number of factors can affect the inhibition performance of a SI, such as hydrodynamics, structure of SI, brine composition such as divalent ions or salinity and temperature conditions;
2. There are two modes of interaction – nucleation inhibition and crystal growth blocking. All scale inhibitors operate through both mechanisms but one can appear more dominant. Phosphonates are less effective at preventing initial crystallisation but very effective at subsequent blocking of active growth sites on crystal surfaces. Polymers are very effective at nucleation inhibition but become consumed over time within the growing crystal lattice. This can be illustrated by the static inhibition efficiency tests via careful monitoring of the IE and [SI]. For instance high IE relates to high [SI] and low IE relates to low [SI];
3. An increase in calcium concentration appears to dramatically improve the performance of phosphonate scale inhibitors with polymeric species being less affected. The presence of magnesium ions is significantly detrimental to the performance of phosphonate type scale inhibitors with polymeric species being less affected;
4. Polymeric species have a greater affinity for calcium than magnesium at all [$Ca^{2+}$] levels. An incompatibility occurs with the polymer PPCA at high levels of [$Ca^{2+}$] leading to a decrease in inhibition efficiency which relates to less SI being present in the solution to protect against scaling as it has dropped out of solution as precipitate;
5. Further studies examining saturation ratio and $Ca^{2+}/Mg^{2+}$ ratio effects on barite inhibition efficiency have identified two different types of behaviour within various phosphonate species where each set can be classified as Type 1 or Type 2 depending on their behaviour, where the classifications are as detailed below;

Type 1 – DETPMP/OMTHP

- Barite IE principally affected by barite SR
- Barite IE affected by brine $Ca^{2+}/Mg^{2+}$ molar ratio is a secondary effect ($Ca^{2+}$ assists and $Mg^{2+}$ 'poisons' inhibition of barite)
- Barite IE performance is better at lower salinities (for the ionic strength range tested here)
- IE tends not to decline very much with time i.e. IE at 2 and 22hrs is similar

Type 2 – HMTPMP/HDMP

- Barite IE is principally affected by brine $Ca^{2+}/Mg^{2+}$ molar ratio ($Ca^{2+}$ assists and $Mg^{2+}$ 'poisons' inhibition of barite)
- Barite IE affected by barite SR as a secondary effect
- Barite IE performance is better at higher salinities (for the ionic strength range tested here)
- IE tends to decline markedly with time i.e. IE much lower at 22hrs compared to 2hrs

6. ESEM images of scale deposits formed in the SI consumption experiments were found to display distinct crystal morphologies for each phosphonate species, such that SEM images could be used as a fingerprint to determine which type of phosphonate had been present in a static inhibition efficiency test;
7. Similar studies, as detailed in point 5 performed for polymeric species again correlates broadly with SR but the $Ca^{2+/}Mg^{2+}$ effect on IE depends on two factors (a) the specific functional groups and atoms that are present (e.g. carboxylate, sulphonate, phosphonate and N, O donor atoms and (b) the abundance of these various functional groups and linking atoms;
8. An additional classification can be added to the Type 1 or 2 SI behaviours as Type A or B depending on compatibility or incompatibility of the SIs in high $[Ca^{2+}]$ brines;

   Type A (more $Ca^{2+}$ compatible) – all phosphonates, SPPCA, PVS, VS-Co, CTP-A, CTP-B

   Type B (less $Ca^{2+}$ compatible) – PPCA, MAT, PFC
9. The need to investigate both homogeneous and heterogeneous nucleation and growth of scale as deposition kinetics can vary, requiring different levels of SI

protection. A scale inhibitor can promote surface growth as its concentration falls below its MIC i.e. [SI] < MIC;

10. It is important to understand the scaling system to be dealt with, over the full range of temperatures to be encountered, in order to identify potential scaling problem areas where sub-MIC SI levels could allow enhanced surface growth. This is particularly significant when considering SI re-treatment for the protection of key components e.g. in ESP's;
11. Deposition data can be related to rate laws 1 and 2 where 'Sulphate Safe Envelopes' can be developed giving a practical approach for addressing the level of sulphate reduction required such that SI squeezes can be avoided. These models can be applied to seeded and un-seeded tests although the seeded test accelerates the kinetics. The highest rate of deposition is for barite seeds (rather than sand) and for a higher surface area over a lower one. The kinetic models developed in this work can be used to predict the actual masses of barite deposited;
12. For the first time, both theoretical and experimental confirmation of how to diagnose and quantify (a) pure adsorption mechanism of SI onto rock or (b) coupled adsorption/precipitation retention has been achieved. The theory is derived and resulting equations solved numerically to predict experimental data with excellent agreement. This adsorption/precipitation model has been incorporated into a SI design tool like SQUEEZE, allowing a better physical description of a squeeze treatment to be achieved. Improved squeeze designs lead to more accurate future predictions of SI returns and better optimised treatments;
13. Amino-propyl cartridges allowed the separation of a sulphonated species from a salty brine system. This had previously been unachievable other than through laborious dialysis techniques. Analysis of these SI products in the field should now be a quicker and more accurate process;
14. The developed Oasis® 2x4 method, although of similar accuracy and repeatability to the C18 and $NH_2$ cartridges, still has a number of advantageous (a) less sample required, (b) less time consuming – 20 samples processes simultaneously cf. 10 and (c) this one method can potentially be used for a variety of different generic types of polymeric SIs;
15. The ICP analysis in the oil phase allowed the direct analysis of ions of interest and SI concentration without the requirement of a partitioning step into water from a non-aqueous treatment. This reduces the potential problems of loss of ions/SI,

giving a more accurate picture of components in each phase. This technique has been particularly useful for analysing core flood returns and closing the mass balance on the oil soluble (or oil dispersed) SI;

16. A Matrix-Matching Hyamine technique was developed which negates the effect of chloride ions on the chelating process of Hyamine and the SI, allowing accurate analysis for low polymeric scale inhibitor concentrations. This is especially suited to a field environment where only a UV spectrometer may be available;
17. A new 'yellow' p-tagged co-polymer can be determined by both ICP and wet chemical techniques which give consistent results between methods;
18. The p-tagged co-polymer was found to have a greater P signal than PPCA which would help with its low end concentration determinations under field conditions where interferences could be present making the analysis more difficult i.e. greater P signal from SI makes it easier to detect from background response;

## 1.6 Future Work

Whilst writing this Thesis, some of my colleagues have already pursued the thesis topics further. The papers containing the further developments are detailed below, alongside the additional future activity, to be performed;

**Effect of Cations on Inhibitor Performance**

- ***Future:*** Investigate the effects of $Ca^{2+}$ and $Mg^{2+}$ on inhibition performance, including the latest results of Shaw, S.S. (2012a, 2012b, 2013a, 2013b) using molecular dynamics modelling

**Use kinetic models and [SI] monitoring for better protection of specific equipment or system areas; ESP, valves**

- ***Future****:* Examine DETPMP, a penta-phosphonate which works through a different SI mechanism, under similar conditions. Observe any enhanced growth behaviour differences when a crystal growth retarder SI is present instead of a nucleation inhibitor

**'Safe envelope approach'; Suggests [$Ba^{2+}$] and [$SO_4^{2-}$] for no squeeze or reduced treatment requirement**

- Calculations adapted for a predictive STR model (Boak, L.S. 2007b) which has been applied in a field situation where possible barite deposition was being observed in gravel packs (Shields, R.S. 2010)
- ***Future:*** Investigations to compare field mass predictions with the model would be useful to identify whether further refinements to the model are required. Another option would be to screen or design scale inhibitor products for a specific desulphation application where long, low scale inhibitor concentrations would be beneficial, such as a hexa-phosphonate species

**Using a new retention model allows better predictions/matches of field data using squeeze software**

- ***Future:*** Investigate the effects of further developments to the model by Ibrahim, J (2012a, 2012b), Sorbie, K.S. (2010, 2012) and Vazquez, O. (2010) by manipulating real field return data for a coupled adsorption/precipitation squeeze treatment and compare the model predictions with the real return profiles

**Improved detection aids for scale inhibitor analysis**

- ***Future:*** Concentrate on automated procedures for SI analysis, such as HPLC and investigate the appropriateness of other 'state of the art' analytical detectors and equipment for the determination of [specific SI species] in solution. Potential techniques could be X-ray Absorption Near Edge Structures (XANES), Extended X-ray Absorption Fine Structure (EXAFS) or X-ray Absorption Fine Structure (XAFS)

## 1.7 Contributions of Author

The contributions of the author to the various papers submitted for this PhD by publication are as follows:

Paper 1: I performed all of the experimental work and analysed the results for this paper, before writing the first draft of the document.

Paper 2: For this paper, I acted as supervisor, discussing the design of the experimental work and the results, before being first reader of the document. I also carried out the ICP analytical work which was essential for this paper.

Paper 3: I designed and performed the experimental work in this paper that investigates the deposition kinetics of barium sulphate scaling under seeded and un-seeded conditions. I was also first author in writing this paper.

Paper 4: Throughout the work programme for this paper, I undertook a laboratory supervision/training role for the student, Mhamed Kahrwad, ensuring that competency of the test procedures was achieved and then adopted for future investigations. I performed most of the required ICP analysis for the student and demonstrated to the student how to manipulate the data. During the submission process of the paper, I was one of the revision readers of the paper and the main corresponding author. I performed the corrections from the peer review process and followed the paper's progress until publication.

Paper 5: I performed and analysed all the experimental work in this paper. I wrote the first draft of this paper and was the corresponding author for the peer review process right through to publication.

Papers 6 and 7: For these 2 papers, I was in a supervisory role as this work followed on directly from my initial work in Paper 1. I trained the student, Scott Shaw in the required techniques and how to analyse the data. I was first reader/editor of each draft paper.

## References


Al-Shaibani, M.: "Coupled Adsorption/Precipitation Modelling of Scale Inhibitor Squeeze Treatments", MSc Petroleum Engineering, Institute of Petroleum Engineering, Heriot-Watt University, 2009.

Alwi, N., Salleh, I.K., Irvine-Fortescue, J., Graham, G.M., Dyer, S., Wright, R, Simpson, C., Kidd, S. and Stalker, R.: "Scale and Scale Inhibitor Challenges for an Alkaline Surfactant Polymer Flood in a Seawater Flooded Reservoir", SPE 164058, SPE International Symposium on Oilfield Chemistry, The Woodlands, Texas, USA, April 2013.

Andersson, G., Molesworth, G., Gonzalez, S.A-H. and Lian, E.: "Innovative Water-Shutoff Solution Enhances Oil Recovery From a West Venezuela Sandstone Reservoir", SPE 111512, International Symposium and Exhibition on Formation Damage, Lafayette, Louisiana, USA, 13-15 February 2008.

Aoun, M., Plasari, E., David, R. and Villermaux, J.: "A Simultaneous Determination of Nucleation and Growth Rates From Batch Spontaneous Precipitation", *Chemical Engineering Science*, 54, 1161-1189, 1999.

Barthorpe, R.T.: "The Dramatic Effect of Certain Divalent Ions Upon Barium Sulphate Inhibition", paper no. 23, NACE Corrosion Conference, Nashville, Tennessee, 27 April – 1 May 1992.

Bedrikovetsky, P., Mackay, E.J., Monteiro, F., Patricio, F and Rosário, F.F.: "Injectivity Impairment Due to Sulphate Scaling During PWRI: Analytical Model", SPE 100512, International Symposium on Oilfield Scale, Aberdeen, UK, 31 May – 1 June 2006.

Bezzera, M.C.M., Rosário, F.F., Rocha, A.A., Sombra, C.L.: "Assessment of Scaling Tendency of Campos Basin Fields Based on the Characterisation of Formation Waters", SPE 87452, 6th International Symposium on Oilfield Scale, Aberdeen, UK, 26-27 May 2004.

Boak, L.S.: "Investigation of the Adsorption and Barium Sulpahte Inhibition Efficiency Properties of Novel Polyethylene Imines With More Conventional Scale Inhibitors", M.Phil Thesis, Department of Petroleum Engineering, Heriot-Watt University, 1996.

Boak, L.S., Graham, G.M. and Sorbie, K.S.: "The Influence of Divalent Cations on the Performance of $BaSO_4$ Scale Inhibitor Species", SPE 50771, SPE International Symposium on Oilfield Chemistry, Houston, Texas, 16-19 February 1999.

Boak, L.S., Graham, G.M. and Hobden, C.M.: "The Effect of a Polymeric and a Phosphonate Scale Inhibitor on the Adherence and Growth of $BaSO_4$ on Hastelloy C276", Paper A1450, 13th International Conference on Crystal Growth, Japan, July 2001.

Boak, L.S., Graham G.M., and Jeannot, M.: "Effect of Corrosion Inhibitor and Scale Inhibitor Additives on Growth of Sulphate Scales at Metal Surfaces" SPE 80394, SPE 5th International Symposium on Oilfield Scale, Aberdeen, UK, 29-30 January 2003.

Boak, L.S., Al-Mahrouqi, H., Mackay, E.J., Inches, C.E., Sorbie, K.S., Bezerra, M.C.M. and Mota, R.O.: "What Level of Sulphate Reduction is Required to Eliminate the need for Scale Inhibitor Squeezing?", SPE 95089, 7th International Symposium on Oilfield Scale, Aberdeen, UK, 11-12 May 2005.

Boak, L.S. and Sorbie, K.S.: "The Kinetics of Sulphate Deposition in Seeded and Unseeded Tests", *SPE Production and Operations*, Vol. 22, Issue No. 4, pp. 442-450, November 2007a.

Boak, L.S., Sorbie, K.S. and Ziadi, C.: "Barite Deposition Kinetic Studies: Flow Cell Experimental Results and Modelling", 18th NIF International Oilfield Chemistry Symposium, Geilo, Norway, 25-28th March 2007b.

Bogaert, P., Berredo, M.C., Jordan, M.M., Frigo, D.M., Morgenthaler, L., Bryson, B. and Afonso, M.: "Scale Inhibitor Squeeze Treatments Deployed from an FPSO in Deepwater, Subsea Fields in the Campos Basin", *SPE Productions & Operations*, pp. 451-471, November 2007.

Bourne, H.M., Heath, S.M. and McKay, S.: "Effective Treatment of Subsea Wells with a Solid Scale Inhibitor System", SPE 60207, International Symposium on Oilfield Scale, Aberdeen, UK, 26-27 January 2000.

Breen, P.J. and Diel, B.N. and Downs, H.H.: "Correlation of Scale Inhibitor Structure with Adsorption Thermodynamics and Performance in Inhibition of Barium Sulfate in Low-pH Environments", SPE 20688, 65th Annual Technical Conference and Exhibition of the Society of Petroleum Engineers, New Orleans, LA, 23-26 September 1990.

Browning, F.H. and Fogler, H.S.: "Precipitation and Dissolution of Calcium-Phosphonates for the Enhancement of Squeeze Lifetimes", SPE 25164, SPE International Symposium on Oilfield Chemistry, New Orleans, LA, USA, 2-5 March 1993.

Bunney, J., Sorbie, K.S. and Jordan, M.M.: "Disequilibria in Fluid/Rock Interactions: Reconciling Experimental and Thermodynamic Coreflooding", Extended Abstract, GEOFLUIDS II Conference, Belfast, 1997.

Busch, K.W., Busch, M.A., Parker, R.E. Darling and McAtee, J.L.: "Studies of a Water Treatment Device That Uses Magnetic Fields", Corrosion, Vol. 42, No. 4, pp. 211-221, April 1986.

Carlberg, B.L.: "Precipitation Squeeze Can Control Scale in High-Volume Wells", Oil and Gas Journal, p152-154, 26 December 1983.

Carlberg, B.L.: "Scale Inhibitor Precipitation Squeeze for Non-Carbonate Reservoirs" SPE 17008, SPE Production Technology Symposium, Lubbock, Texas, 16-17 November 1987.

Charleston, J.: "Scale Removal in the Verdin, Manitoba Area", SPE 2160, 43rd Annual Fall Meeting, Houston, Texas, 1970.

Chekani, M. and Mackay, E.J.: "Impact on Scale Management of the Engineered Depressurisation of Waterflooded Reservoirs: Risk Assessment Principles and Case Study", SPE 86472, SPE International Symposium and Exhibition on Formation Damage, Lafayette, Louisiana, 18-20 February 2004.

Chemguide.: http://www.chemguide.co.uk/inorganic/group2/solubility.html

Chen, P., Hagen, T, Bourne, H, Turner, K, Nielsen, F.M., Rian, M. and Haldoupis, A.: "The Challenge of Squeezing a Water Sensitive HP/HT Reservoir – Lab and Field Experiences with a Novel Non-Aqueous Inhibitor/Squeeze Enhancer Package", SPE 87435, International Symposium on Oilfield Scale, Aberdeen, UK, 26-27 May 2004.

Chen, T., Neville, N., Sorbie, K.S. and Zhong, Z.: "*In-Situ* Monitoring Of The Inhibiting Effect of DETPMP on $CaCO_3$ Scale Formation by Synchrotron X-Ray Diffraction", Paper No. 07053, NACE Corrosion 2007, Conference and Expro, 2007.

Chen, H.J., Henrichsen, C.J., Burnside, C.A., Widener, M.: "Assessment of Barite Scaling Potentials, Sulfate Removal Options and Chemical Treating Strategies for the Tombua-Landana Development", SPE 106480, International Symposium on Oilfield Chemistry, Houston, Texas, USA, 27 February – 2 March 2007.

Cheong, W., Neville, A., Gaskell, P.H. and Abbott, S.: "Using Nature to Provide Solutions to Calcareous Scale Deposition", SPE 114082, SPE International Oilfield Scale Conference, Aberdeen, UK, 28-29 May 2008.

Coetzee, P.P., Yacoby, M., Howell, S. and Mubenga, S.: "Scale Reduction and Scale Modification Effects Induced by Zn and Other Metal Species in Physical Water Treatment", Water SA, Vol. 24, No. 1, pp. 77-84, January 1998.

Coey, J.M.D. and Cass, C.: "Magnetic Water Treatment", *Journal of Magnetism and Magnetic Materials*, Vol. 209, pp. 71-74, 2000.

Collins, I.R., Jordan, M.M., Feasey, N. and Williams, G.D.: "The Development of Emulsion-Based Production Chemicals Deployment Systems", SPE 65026, International Symposium on Oilfield Chemistry, Houston, Texas, 13-16 February 2001.

Collins, I.R.: "A New Model for Mineral Scale Adhesion on Surfaces", SPE 74655, SPE 4th International Symposium on Oilfield Scale, Aberdeen, UK, 30-31 January 2002.

Collins, I.R., Stalker, R. and Graham, G.M.: "Sulphate Removal for Barium Sulphate Scale Mitigation a Deepwater Subsea Production System", SPE 87465, 6th International Symposium on Oilfield Scale, Aberdeen, UK, 26-27 May 2004.

Cruise, D.S., Davis, D.L. and Elliot, R.H.: "Use of Continuous Coil Tubing for Subsurface Scale and Corrosion Treating – Rangely Weber Sand Unit", SPE 11853, Rocky Mountain Regional Meeting, Salt Lake City, UT, 23-25 May, 1983.

Cushner, M.C., Prybylinski, J.L. and Ruggeri, J.W.: "How Temperature and pH Affect the Performance of Barium Sulphate Inhibitors", Paper no. 428, NACE Corrosion 88, St Louis, Missouri, March 1988.

Dai, H., Shi, W., Kan, A.T., Zhang, N. and Tomson, M.: "Thermodynamic Model Improvements for Common Minerals at High Temperature, High Pressure and High TDS with Mixed Salts", SPE 164045, SPE International Symposium on Oilfield Chemistry, The Woodlands, Texas, USA, April 2013.

Daminov, A., Ragulin, V. and Voloshin, A.: "Mechanism Formations of Corrosion Damage of Inter Equipment in Wells by Continuous Scale Inhibitor Dosing Utilising Surface Dosing Systems: Testing Scale and Corrosion Inhibitors", SPE 100476, SPE International Oilfield Corrosion Symposium, Aberdeen, UK, 30 May 2006.

Donaldson, J. and Grimes, S.: "Control of Scale in Sea Water Applications by Magnetic Treatment of Fluids", SPE 16540/1, Offshore Europe, Aberdeen, 8-11 September 1987.

Donaldson, J. and Grimes, S.: "Lifting the Scales from our Pipes", New Scientist, pp. 43-46, 18 February 1988.

Duan, W., Oota, H and Swada, K.: "Stability and Structure of Ethylenedinitrilopoly (methylphosphonate) Complexes of the Alkaline-Earth Metal ions in Aqueous Solution", *J. Chem. Soc., Dalton Trans.*, 3075-3080, 1999.

Dunn, K., Daniel, E., Shuler, P.J., Chen, H.J., Tang, Y. and Fu Yen, T.: "Mechanisms of Surface Precipitation and Dissolution of Barite: A Morphology Approach", Journal of Colloid and Interface Science, 214, 427-437, 1999.

Dyer, S.J., Graham, G.M., Shone, P. and Sorbie, K.S.: "Scale Control Under HP/HT Reservoir Conditions", 9th NIF International Symposium on Oilfield Chemicals, geilo, Norway, 22-25 March 1998.

Dyer, S.J., Graham, G.M. and Sorbie, K.S.: "Factors Affecting the Thermal Stability of Conventional SI's for Application in High Pressure/High Temperature Reservoirs", SPE 50717, SPE International Symposium on Oilfield Chemistry, Houston, Texas, 16-19 Feb 1999.

Eroini, V, Neville, A., Kapur, N. and Euvrard, M.: "Preventing Scale Formation Using Modified Surfaces", Paper no. 11344, NACE Corrosion 2011 Conference and Expro.

El Attar Sofi, Y., Carquille, C., Lamarche, J.M. and Foissy, A.: "Influence of Calcium and Phosphate Ions on the Adsorption of Partially Hydrolyzed Polyacrylamides on $TiO_2$ and $CaCO_3$", *Progress in Colloid & Polymer Science*, 82, 43-51, 1990.

Farshad, F.F., Linsley, J., Kuznetsov, O. and Vargas, S.: "The Effects of Magnetic Treatment on Calcium Sulfate Scale Formation", SPE 76767, SPE Western

Regional/AAPG Pacific Section Joint Meeting, Anchorage, Alaska, USA, 20-22 May 2002.

Furtado, C.J.A., Siqueira, A.G., Souza, A.L.S., Correa, A.C.F. and Mendes, R.A.: "Produced Water Reinjection in Petrobras Fields: Challenges and Perspectives", SPE 94705, SPE Latin American and Caribbean Petroleum Engineering Conference, Rio de Janeiro, Brazil, 20-23 June 2005.

Gabrielli, C., Keddam, M., Khalil, A., Rosset, R and Zidoune, M.: "Study of Calcium Carbonate Scales by Electrochemical Impedance Spectroscopy", Electrochemica Acta, Vol. 42, No. 8, pp1207-1218, 1997.

Garcia, C., Courbin, G., Noik, C., Ropital, F. and Fiaud, C.: "Development of the Electrochemical Quartz Crystal Microbalance to Control Carbonate Scale Deposit", Paper no. 114, CORROSION 99, Houston, 1999.

Gdanski, R.D. and Funkhouser, G.P.: "Successful Model of the Kinetic Release of a Phosphonate Scale Inhibitor", NIF International Oilfield Chemistry Symposium, Geilo, Norway, 1-4 April 2001.

Gehr, R., Zhai, Z.A., Finch, J.A. and Rao, R.: "Reduction of Soluble Mineral Concentrations in $CaSO_4$ Saturated Water Using a Magnetic Field", Wat. Res., Vol. 29, No. 3, pp. 933-940, 1995.

Goodwin, N.J., Svela, O.G., Olsen, J.H., Tjpmsland, T., Hustad, B.M. and Graham, G.M.: "Qualification Procedure for Continuous Injection of Chemicals in the Well – Method Development", SPE 154934, SPE International Conference and Exhibition on Oilfield Scale, Aberdeen, UK, 30-31 May 2012.

Graham, A.L., Vieille, E., Neville, A., Boak, L.S. and Sorbie, K.S.: "Inhibition of $BaSO_4$ at a Hastelloy Metal Surface and in Solution: The Consequences of Falling Beneath the Minimum Inhibitor Concentration (MIC)", SPE 87444, $6^{th}$ International Symposium on Oilfield Scale, Aberdeen, UK, 26-27 May 2004.

Graham, A.L., Boak, L.S., Neville, A. and Sorbie. K.S.: "How Minimum Inhibitor Concentration (MIC) and Sub-MIC Concentrations Affect Bulk Precipitation and Surface Scaling Rates", SPE 93311, 2005 SPE International Symposium on Oilfield Chemistry, Houston, Texas, U.S.A., 2 – 4 February 2005 and Vol. 21, Issue No. 1, pp. 19-25, *SPE Production & Operations*, February 2006.

Graham, G.M., Sorbie, K.S., Yuan, M.D. and Todd, A.C.: “New Scale Inhibitors for Future Oilfield Applications”, Advances in Solving Oilfield Scaling Problems, Aberdeen, UK, 7-8 October 1992.

Graham, G.M.: “A Mechanistic Examination of the Factors Influencing Downhole $BaSO_4$ Oilfield Scale Inhibitors and the Design of New Species”, PhD Thesis, Department of Petroleum Engineering, Heriot-Watt University, 1994a.

Graham, G.M. and Sorbie, K.S.: “The Effect of Molecular Weight on the Adsorption/Desorption Characteristics of Polymeric Scale Inhibitors on Silica Sand and in Sandstone Cores”, Paper no. 50, NACE Annual Conference, Baltimore, Maryland, 28 February – 4 March 1994b.

Graham, G.M., Sorbie, K.S., Boak, L.S., Taylor, K. and Blilie, L.: “Development and Application of Accurate Detection and Assay Techniques for Oilfield Scale Inhibitors in Produced Water Samples”, SPE 28997, SPE International Symposium on Oilfield Chemistry, San Antonio, Texas, USA, 14-17 February 1995.

Graham, G.M., Jordan, M.M. and Sorbie, K.S.:” How Scale Inhibitors Work and How this Affects Test Methodology”, 3rd International Conference on Advances in Solving Oilfield Scaling, IBC Technical Services Ltd., Aberdeen, 22-23 January 1997a.

Graham, G.M., Boak, L.S. and Sorbie, K.S.: “The Influence of Formation Calcium on the Effectiveness of Generically Different Barium Sulphate Oilfield Scale Inhibitors”, SPE 37273, SPE International Symposium on Oilfield Chemistry, Houston, Texas, 18-21 February 1997b.

Graham, G.M., Dyer, S.J., Sorbie, K.S., Sablerolle, W.R., Shone, P. and Frigo, D.: “SI Selection for Continuous and Downhole Squeeze Application in HP/HT Conditions”, SPE 49197, SPE Annual Technical Conference and Exhibition, New Orleans, Louisiana, 27-30 September 1998.

Graham, G.M., Dyer, S.J. and Shone, P.: “Potential Application of Amine Methylene Phosphonate based Inhibitor in HP/HT Environments for Improved Carbonate SI Performance”, SPE 60217, SPE 2nd International Symposium on Oilfield Scale, Aberdeen, 26-27 January 2000.

Graham, G.M., Boak, L.S. and Hobden, C.M.: "Examination of the Effect of Generically Different Scale Inhibitor Species (PPCA and DETPMP) on the Adherence and Growth of Barium Sulphate Scale on Metal Surfaces", SPE 68298,

SPE 3rd International Symposium on Oilfield Scale, Aberdeen, Scotland, 30-31 January 2001a.

Graham, G.M., Frigo, D.M., McCracken, I.R., Graham, G.C., Davidson, W.J., Kapusta, S. and Shone, P.: "The Influence of Corrosion Inhibitor/SI Interference on the Selection of Chemical Treatments under Harsh (HP/HT/HS) Reservoir Conditions", SPE 68330, SPE 3rd International Symposium on Oilfield Scale, Aberdeen, 30-31 January 2001b.

Graham, G.M., Mackay, E.J., Wattie, I and Boak, L.S.: "Scale Inhibitor Selection Criteria for Downhole (SQUEEZE) Application in a High Volume Horizontal Well in a Fractured Chalk Reservoir", SPE 65025, International Symposium on Oilfield Chemistry, Houston, Texas, 13-16 February 2001c.

Graham, G.M., Collins, I.R., Stalker, R. and Littlehales, I.J.: "The Importance of Appropriate Laboratory Procedures for the Determination of Scale Inhibitor Performance", SPE 74679, SPE Oilfield Scale Symposium, Aberdeen, UK, 30-31 January 2002a.

Graham, G.M. and McMahon, C.P.: "The Effect on Scale Inhibitor Performance Against Bulk (Homogeneous) and Surface (Heterogeneous) Scale Nucleation and Growth by the Addition of Film Forming Corrosion Inhibitors", Paper No. 02315, NACE CORROSION/2002, Colorado, April 2002b.

Graham, G.M., Mackay, E.J., Dyer, S.J. and Bourne, H.M.: "The Challenges for Scale Control in Deepwater Production Systems – Chemical Inhibition and Placement Challenges", Paper No. 02316, NACE CORROSION/2002, Colorado, April 2002c.

Graham, G.M., Boak, L.S. and Sorbie, K.S.: "The Influence of Formation Calcium and Magnesium on the Effectiveness of Generically Different Barium Sulphate Oilfield Scale Inhibitors", *SPE Production and Facilities*, Vol. 18, Issue No. 1, pp. 28 - 44, February 2003.

Graham, G.M. and Collins, I.R.: "Assessing Scale Risks and Uncertainties for Subsea Marginal Field Developments", SPE 87460, 6th International Symposium on Oilfield Scale, Aberdeen, UK, 26-27 May 2004.

Griffiths, D.W., Roberts, S.D. and Liu, S-T.: "Inhibition of Calcium Sulfate Dihydrate Crystal Growth by Phosphonic Acids – Influence of Inhibitor structure and Solution pH", SPE 7862, SPE International Symposium on Oilfield and Geothermal Chemistry, Houston, 22-24 January 1979.

Griffin, J.R., Johnstone, J.R., Cotter, T.E. and O'Brien, A.E.: "Factors Affecting the Stability of Scale Inhibitors Used for Capillary Injection in High Temperature Wells", SPE 164128, SPE International on Oilfield Chemistry, The Woodlands, Texas, USA, 8-10 April 2013.

Guan, H.: "Carbonate Scaling Prediction: The Importance of Valid Data Input", Paper No. 10132, NACE Corrosion Conference and Expro, 2010.

Hardy, J.A., Barthorpe, R.T., Plummer, M.A. and Rhudy, J.S.: "Scale Control in the South Brae Field", SPE 25141-PA, SPE Production & Facilities, Vol. 9, No. 2, p127-131, May 1994.

Hasson, D., Bramson, D., Limoni-Relis, B., Semait, R.: "Influence of the Flow System on the Inhibitory Action of $CaCO_3$ Scale Prevention Additives", Desalination, 108, 67-79, 1996.

Higashitani, K., Kage, A., Katamura, S., Imai, K. and Hatade, S.: "Effects of a Magnetic Field on the Formation of $CaCO_3$ Particles", Journal of Colloid and Interface Science, Vol. 156, pp. 90-95, 1993.

His, C.D. and McCracken, I.R.: "Stopped-Flow Spectrophotometry – A Novel Method to Evaluate Scale Inhibitor Performance", Paper no. 30, NACE Corrosion 92, Nashville, Tennessee, 27 April-1 May 1992.

Howard, G.J. and McConnell, P.: "Adsorption of Polymers at the Solution-Solid Interface: I. Polyethers on Silica", Journal of Physical Chemistry, Vol 71, no. 9, p2974-2980, August 1967.

Hustad, B.M., Svela, O.G., Olsen, J.H., Ramstad, K. and Tjomsland, T.: "Downhole Chemical Injection Lines – Why Do They Fail? Experiences, Challenges and Application of New Test Methods", SPE 154967, SPE International Conference and Exhibition on Oilfield Scale, Aberdeen, UK, 30-31 May 2012.

Iler, R.K.: "The Chemistry of Silica", A Wiley-Interscience Publication, New York, Chapter 4-6, 1979, ISBN-10: 047102404X, ISBN-13: 978-0471024040.

Ibrahim, J., Sorbie, K.S. and Boak, L.S.: "Coupled Adsorption/Precipitation Equipments: 1. Static Results", SPE 155109, SPE International Conference on Oilfield Scale, Aberdeen, UK, 30-31 May 2012a.

Ibrahim, J., Sorbie, K.S. and Boak, L.S.: "Coupled Adsorption/Precipitation Equipments: 2. Non-Equilibrium Sand Pack Treatment", SPE 155110, SPE International Conference on Oilfield Scale, Aberdeen, UK, 30-31 May 2012b.

Inches, C.E., Sorbie, K.S. and El Doueiri, K.: "Green Inhibitors: Mechanisms in the Control of Barium Sulphate Scale", Paper No. 06485, 61st Annual Conference and Exposition, Corrosion NACExpo 2006, San Diego, California, USA, 12-16 March, 2006.

Jordan, M.M., Sorbie, K.S. et al.: "The Effects of Clay Minerals, pH, Calcium and Temperature on the Adsorption of Phosphonate SI's onto Reservoir Core and Mineral Separates", NACE Corrosion /94, Baltimore, Maryland, 28 Feb-4 March 1994.

Jordan, M.M., Graff, C.J. and Cooper, K.N.: "Development and Deployment of a Scale Squeeze Enhancer and Oil-Soluble Scale Inhibitor to Avoid Deferred Oil Production Losses During Squeezing Low-water Cut Wells, North Slope, Alaska", SPE 58725, SPE International Symposium on Formation damage control, Lafayette, Louisiana, 23-24 February 2000.

Jordan, M.M., Sjuraether, K., Collins, I.R., Feasey, N.D. and Emmons, D.: "Life Cycle Management of Scale Control within the Subsea Fields and its Impact on Flow Assurance, Gulf of Mexico and the North Sea Basin", SPE 71557, SPE Annual Technical Conference and Exhibition, New Orleans, Louisiana, 30 Sept – 3 Oct 2001.

Jordan, M.J., Sjursaeter, K. and Collins, I.: "Scale Control within North Sea Chalk/Limestone Reservoirs. The Challenge of Understanding and Optimising Chemical Placement Methods and Retention Mechanism: Laboratory to Field", Paper No. 04389, NACE Corrosion 2004.

Jordan, M.M., Collins, I.R. and Mackay, E.J.: "Low-Sulfate Seawater Injection for Barium Sulfate Scale Control: A Life-of-Field Solution to a Complex Challenge", SPE 98096, International Symposium and Exhibition on Formation Damage Control, Layfayette, Louisiana, 15-17 February 2006.

Kahrwad, M., Sorbie, K.S., Boak, L.S.: "Coupled Adsorption/Precipitation of Scale Inhibitors: Experimental Results and Modelling", *SPE Production and Operations*, Vol. 24, Issue No. 3, pp.481-491, August 2009.

Kan, A, Yan, L., Bedient, P.B., Oddo, J. E. and Tomson, M.B.: "Sorption and Fate of Phosphonate Scale Inhibitors in the Sandstone Reservoir – Studied by Laboratory Apparatus With Core Material", SPE 21714, SPE Production Operations Symposium, Oklahoma City, Oklahoma, 7-9 April 1991.

Kan, A., Fu, G., Shen, D., Al-Saiari, H. And Tomson, M.B.: "Enhanced Inhibitor Treatment with Addition of Transition Metal ions", SPE 114060, SPE International Oilfield Scale Conference, Aberdeen, UK, 28-29 May 2008.

Kan, A.T. and Tomson, M.B.: "Scale Prediction for Oil and Gas Production", *SPE Journal*, pp. 362-378, June 2012.

Kan, A.T., Zhang, N., Shi, W., Wang, K., Wang, L., Yan, C., Yan, F. and Tomson, M.B.: "Interrelationship of $CO_2$, Weak Acids, Bases and pH in Scale Prediction and Control", SPE 164127, SPE International Symposium on Oilfield Chemistry, The Woodlands, Texas, USA, April 2013.

King, G.E. and Wardon, S.L.: "Introductory Work in Scale Inhibitor Squeeze Performance: Core Test and Field Results", SPE 18485, SPE International Symposium on Oilfield Chemistry, Houston, Texas, 8-10 February 1989.

Kronenberg, K.J.: "Experimental Evidence for Effects of Magnetic Fields on Moving Water", *IEEE Transactions on Magnetics*, Vol. MAG-21, No. 5, September 1985.

Labille, S., Neville, A., Graham, G.M. and Boak, L.S.: "An Assessment of Adhesion of Scale and Electrochemical Pre-treatment for the Prevention of Scale Deposition on Metal Surfaces", SPE 74676, SPE International Symposium on Oilfield Scale, January 2001 and Journal of Petroleum Technology, pp.51-52, Dec 2002.

Lauer, R.S.: "The Use of High Performance Polymeric Coatings to Mitigate Corrosion and Deposit Formation in Pipeline Applications", Paper No. 07028, NACE Corrosion 2007 Conference and Expro.

Liu, S.T., Nancollas, G.H. and Gasiecki, E.A.: "Scanning Electron Microscopic and Kinetic Studies of the Crystallisation and Dissolution of Barium Sulfate Crystals", Journal of Crystal Growth, 33, p11-20, 1976.

Mackay, E.J., Matharu, A.P., Sorbie, K.S., Jordan, M.M. and Tomlins, R.: "Modelling of Scale Inhibitor Treatments in Horizontal Wells: Application to the Alba Field", SPE 39452, SPE International Symposium on Formation Damage Control, Lafayette, Lousiana, 18-19 February 1998.

Mackay, E.J. and Sorbie, K.S.: "Brine Mixing in Waterflooded Reservoirs and the Implications for Scale Prevention", SPE 60193, 2nd SPE International Symposium on Oilfield Scale, Aberdeen, UK, 26-27 January 2000.

Mackay, E.J. and Graham, G.M.: "The Use of Flow Models in Assessing the Risk of Scale Damage", SPE 80252, SPE International Symposium on Oilfield Chemistry, Houston, Texas, USA, 20-21 February 2003a.

Mackay, E.J.: "Predicting *In Situ* Sulphate Scale Deposition and the Impact on Produced Ion Concentrations", Trans IChemE, Vol 81, Part A, p326-332, March 2003b.

Mackay, E.J., Jordan, M.M. and Torabi, F.: "Predicting Brine Mixing Deep Within the Reservoir and the Impact on Scale Control in Marginal and Deepwater Developments", SPE 73779, SPE International Symposium and Exhibition on Formation Damage Control, Lafayette, Louisiana, 20-21 February 2002 and SPE 85104, SPE Production and Facilities, 18, (3), 210-220, August 2003c.

Mackay, E.J. and Jordan, M.M.: "SQUEEZE Modelling: Treatment Design and Case Histories", SPE 82227, SPE European Formation Damage Conference, The Hague, The Netherlands, 13-14 May 2003d.

Mackay, E.J., Jordan, M.M., Feasey, N.D., Shah, D., Kumar, P and Ali, S.A.: "Integrated Risk Analysis for Scale Management in Deepwater Developments", SPE 87459, 6th International Symposium on Oilfield Scale, Aberdeen, UK, 26-27 May 2004.

Mackay, E.J.: "The Application of Reservoir Simulation Calculations to Oilfield Scale Management", PhD Thesis, Institute of Petroleum Engineering, Heriot-Watt University, August 2005.

Mackay, E.J.: "Limiting Scale Risk at Production Wells by Management of PWRI Wells", SPE 96741, International Symposium on Oilfield Chemistry, Houston, Texas, USA, 28 February – 2 March 2007.

Malandrino, A., Yuan, M.D., Sorbie, K.S. and Jordan, M.M.: "Mechanistic Study and Modelling of Precipitation Scale Inhibitor", SPE 29001, SPE International Symposium on Oilfield Chemistry, San Antonio, Texas, 14-17 February 1995.

McKeen, L.W., Hofmans, J. and Nelissen, J.: "Engineered Internal Downhole Coating Solutions for Corrosion and Deposition Control in Downhole Production

Tubulars", SPE 161204, Abu Dhabi International Petroleum Exhibition and Conference, Abu Dhabi, UAE, 11-14 November 2012.

McTeir, M.D.K., Ravenscroft, P.D. and Rudkin, C.: "Modified Methods for the Determination of Polyacrylic/Phosphinopolycarboxylic Acid and Polyvinylsulphonic acid Scale Inhibitors in Oilfield Brines", SPE 25160, SPE International Symposium on Oilfield Chemistry, New Orleans, LA, 2-5 March, 1993.

Mendoza, A., Graham, G.M. and Sorbie, K.S.: "Sulphate Scale Dissolution: Examination of the Factors Controlling the Effectiveness of EDTA and DTPA based on Scale Dissolvers and their Comparative Effectiveness against Different Sulphate Minerals", 10th NIF International Oilfield Chemical Symposium, Fagarnes, Norway, 28 Feb-3 March 1999.

Meric, C. and Sanchez, A.: "Compatibility of Corrosion and Scale Inhibitors in Simulated Petroleum Production Sweet Corrosion System", Revista Tecnica Intevep 5 (2), 189-195, July 1985.

Meyers, K.O., Skillman, H.L. and Herring, G.D.: "Control of Formation Damage at Prudoe Bay, Alaska, by Inhibitor Squeeze Treatment", Journal of Petroleum Technology, pp.1019-1034, June 1985.

Murtala, M.A.: "Characterization, Modelling, Prediction and Inhibition of Naphthenate Deposits in Oilfield Production", PhD Thesis, Institute of Petroleum Engineering, Heriot-Watt University, September 2010.

Morizot, A.P., Neville, A. and Hodgkiess, T.: "Studies of the Deposition of $CaCO_3$ on a Stainless Steel Surface by a Novel Electrochemical Technique", Journal of Crystal Growth, 198/199, 738-743, 1999.

Morizot, A., Neville, A.: "A Novel Approach for Monitoring $CaCO_3$ and $BaSO_4$ Scale Formation", SPE 60189, 2nd International Symposium on Oilfield Scale, Aberdeen, UK, 26-27 January 2000a.

Morizot, A.P., Neville, A.: "A Study of Inhibitor Film Formation Using an Electrochemical Technique", Paper No. 108, Annual Spring Meeting of NACE International, CORROSION 2000, Orlando, USA, 2000b.

Morizot, A.P. and Neville, A.: "Insights into Electrodeposition of an Inhibitor Film and its Inhibitive Effects on $CaCO_3$ Deposition", Journal of Colloid and Interface Science, 245, 40-49, 2002.

Mota, R.O., Bezerra, M.C.M., Rosario, F.F. and Paris, F.: "Forecast and Alternative Analysis for Sulphate Removal or Chemical Treatments for Barium and Strontium Scale Deposition – Offshore Brazil", SPE 87464, 6th International Symposium on Oilfield Scale, Aberdeen, UK, 26-27 May 2004.

NACE Standard TM0197-97: "Laboratory Screening Test to Determine the Ability of scale Inhibitors to Prevent the Precipitation of Barium Sulphate and/or Strontium Sulphate from Solution (for Oil and Gas Production Systems)", Item no. 21228, Nace International, 1997.

Nancollas, G.H.: "Oilfield Scale: Physical Chemical Study of its Formation & Prevention", International Symposium on Chemicals in the Oil Industry, UK, 143-164, 1985.

Oddo, J.E. and Tomson, M.B.: "The Solubility and Stochiometry of Calcium-Diethylenetriaminepenta (methylene phosphonate) at 70°C in 2M Brine Solution @ 4.7-9 pH", GeoChem Science, p527-532, 1990.

Olson, J.B., Moore, D.C. and Holland-Jones, N.: "A Temperature Activated Extended Lifetime Scale Inhibitor Squeeze System", Paper no. 25, NACE Annual Conference, Nashville, TN, 27 April – 1 May 1992.

Olsen, J.H.: "Statoil Experiences and Consequences Related to Continuous Chemical Injection", SPE 146625, SPE Annual Technical Conference and Exhibition, Denver, Colorado, USA, 30 October – 2 November 2011.

Pardue, J.E.: "A New Inhibitor for Scale Squeeze Applications", SPE 21023, SPE International Symposium on Oilfield Chemistry, Anaheim, California, 20-22 February 1991.

Patroni Zavala, J.A., Mackay, E.J., Vazquez, O., Boak, L.S., Singleton, M. and Ross, G.: "The Cost and Value of Field, Laboratory and Simulation Data for Validating Scale Inhibitor Treatment Models", SPE 114106, SPE 9th International Conference on Oilfield Scale, Aberdeen, UK, 28-29 May 2008.

Petrotech a.s Knowledge: "Multiscale", P.O. Box 575, N-5501, Haugesund, Norway, 1998.

Popov, K., Rönkkömäki, H and Lajunen, L.H.J.: "Critical Evaluation of Stability Constants of Phosphonic Acids", Pure Appl.Chem., Vol. 73, No. 10, pp.1641-1677, 2001.

Pritchard, A.M., Cowie, L., Goulding, J.R., Graham, G., Greig, A.C., Hamblin, B.M., Hunton, A. and Terry, S.: "Test Methods for Calcium Carbonate Scale Inhibitors", RSC Chemistry in the Oil Industry III, Manchester, UK, 19-20 April 1988.

Quddus, A. and Allam, I.M.: "$BaSO_4$ Scale Deposition on Stainless Steel", Desalination, 127, p219-224, 2000.

Ragulin, V.V., Markelov, D.V., Voloshin, A.I., Matyash, S.E. and Mikhailov, A.G.: "The Problem of Scaling and Ways to Solve it in the Oilfields of Rosneft Oil Co.", SPE 104354, SPE Russian Oil and Gas Technical Conference and Exhibition, Moscow, Russia, 3-6 October 2006.

Ramsey, J.E. and Cenegy, L.M.: "A Laboratory Evaluation of Barium Sulfate Scale Inhibitors at Low pH for Use in Carbon Dioxide EOR Floods", SPE 14407, 60$^{th}$ SPE Annual Technical Conference, Las Vegas, NV, 22-25 September 1985.

Ramstad, K., Rohde, H.C., Tydal, T. And Christensen, D.: "Scale Squeeze Evaluation Through Improved Sample Preservation, Inhibitor Detection and Minimum Inhibitor Concentration Monitoring", Vol. 24, No. 4, *SPE Production and Operations*, pp.530-542, November 2009.

Sánchez-Moreno, MJ., Fernández-Botello, A., Gómez-Coca, R.B., Griesser, R., Ochocki, J., Kotynski, A., Nicolós-Gutiérrez, J., Moreno, V. and Sigel, H.: "Metal Ion-Binding Properties of (1*H*-Benzimidazol-2-yl-methyl) phosphonate ($Bimp^{2-}$) in Aqueous Solution. Isomeric Equilibria, Extent of Chelation and a New Quantification Method for the Chelate Effect", Inorganic Chemistry, Vol.43, No. 4, pp.1311-1322, 2004.

Sawada, K, Miyagawa, T., Sakaguchi, T and Doi, K.: "Structure and Thermodynamic Properties of Aminopoly-phosphonate Complexes of the Alkaline-Earth Metal Ions", *J. Chem. Soc., Dalton Trans.*, 3777-3784, 1993.

Shaw, S.S., Sorbie, K.S. and Boak, L.S.: "The Effects of Barium Sulphate Saturation Ratio, Calcium and Magnesium on the Inhibition Efficiency: I Phosphonate Scale Inhibitors", SPE 130373, SPE International Conference on Oilfield Scale, Aberdeen, UK, 26-27 May 2010a.

Shaw, S.S., Sorbie, K.S. and Boak, L.S.: "The Effects of Barium Sulphate Saturation Ratio, Calcium and Magnesium on the Inhibition Efficiency: II Polymeric Scale Inhibitors", SPE 130374, SPE International Conference on Oilfield Scale, Aberdeen, UK, 26-27 May 2010b.

Shaw, S.S. and Sorbie, K.S.: "The Effect of pH on Static Barium Sulphate Inhibition Efficiency and Minimum Inhibitor Concentration of Generic Scale Inhibitors", SPE 155094, SPE International Conference on Oilfield Scale, Aberdeen, UK, 30-31 May 2012a.

Shaw, S.S., Welton, T.D. and Sorbie, K.S.: "The Relation between Barite Inhibition by Phosphonate Scale Inhibitors and the Structures of Phosphonate-Metal Complexes", SPE 155114, SPE International Conference on Oilfield Scale, Aberdeen, UK, 30-31 May 2012b.

Shaw, S.S. and Sorbie, K.S.: "Structure, Stoichiometry and Modelling of Calcium Phosphonate Scale Inhibitor Complexes for Application in Precipitation Squeeze Processes", SPE 164051, SPE International Conference on Oilfield Scale, Texas, USA, 8-10 April 2013a.

Shaw, S.S. and Sorbie, K.S.: "Scale Inhibitor Consumption in long-Term Static Barium Sulphate Inhibition Efficiency Tests", SPE 164052, SPE International Conference on Oilfield Scale, Texas, USA, 8-10 April 2013b.

Shen, D., Fu, G., Al-Saiari, H., Kan, A.T. and Tomson, M.B.: "Seawater Injection, Inhibitor Transport, Rock-Brine Interactions and $BaSO_4$ Scale Control during Seawater Injection", SPE 114062, SPE International Oilfield Conference, Aberdeen, UK, 28-29 May 2008.

Shields, R., Bourne, H, Vazquez, O., Sorbie, K.S. and Singleton, M.: "Dynamic Scaling Evaluation in Gravel Packs using Low-Sulphate Seawater", SPE 128002, SPE International Symposium and Exhibition on Formation Damage Control, Lafayette, Louisiana, USA, 10-12 February 2010.

Simpson, C.M., Graham, G.M., Collins, I.R., McElhiney, J. and Davis, R.: "Sulfate Removal for $BaSO_4$ Scale Mitigation – Kinetics vs. Thermodynamic Controls in Mildly Oversaturated Conditions", SPE 95082, SPE International Symposium on Oilfield Scale, Aberdeen, UK, 11-12 May 2005.

Sorbie, K.S., Yuan, M.D., Chen, P., Todd, A.C. and Wat, R.M.S.: "The Effect of pH on the Adsorption and Transport of Phosphonate Scale Inhibitor Through Porous

Media", SPE 25165, SPE International Symposium on Oilfield Chemistry, New Orleans, La, USA, 2-5 March 1988.

Sorbie, K.S, Yuan, M.D. and Todd, A.C.: "The Modelling and Design of SI Squeeze Treatments in Complex Reservoirs", SPE 21024, SPE Int. Symposium on Oilfield Chemistry, Anaheim, California, 20-23 Feb 1991.

Sorbie, K.S., Wat, R.S. and Todd, A.C.: "Interpretation and Theoretical Modelling of Scale Inhibitor/Tracer Corefloods", SPE Production Engineering, 7, (3), 307-312, August 1992a or Trans., AIME, 293, SPE-20687-PA. DOI: 10.2118/20687-PA.

Sorbie, K.S., Yuan, M.D., Graham, G.M. and Todd, A.C.: "Appropriate Laboratory Evaluation of Oilfield Scale Inhibitors", Advances in Solving Oilfield Scaling Problems, IBC Ltd., Aberdeen, 7-8 October 1992b.

Sorbie, K.S., Jiang, P., Yuan, M.D., Chen, P., Jordan, M.M. and Todd, A.C.: "The Effect of pH, Calcium and Temperature on the Adsorption of Inhibitor onto Consolidated and Crushed Sandstone", SPE 26605, SPE 68th Annual Technical Conference, Houston, Texas, 1993.

Sorbie, K.S., Yuan, M.D. and Jordan, M.M.: "Application of a Scale Inhibitor squeeze Model to Improve Field Squeeze Treatment Design", SPE 28885, European Petroleum Conference, London, UK, 25-27 October 1994.

Sorbie, K.S. and Laing, N.: "How Scale Inhibitors Work: Mechanisms of Selected Barium Sulphate Scale Inhibitors Across a Wide Temperature Range", SPE 87470, SPE International Symposium on Oilfield Scale, Aberdeen, UK, 26-27 May 2004.

Sorbie, K.S. and Gdanski, R.D.: "A Complete Theory of Scale-Inhibitor Transport and Adsorption/Desorption in Squeeze Treatments", SPE 95088, SPE International on Oilfield Scale, Aberdeen, UK, 11-12 May 2005.

Sorbie, K.S. and Boak, L.S. (Editors): "Flow Assurance and Scale Team (FAST) Laboratory Procedures Manual", Institute of Petroleum Engineering, Heriot-Watt University, 2006.

Sorbie, K.S.: "A General Coupled Kinetic Adsorption/Precipitation Transport Model for Scale Inhibitor Retention in Porous Media: I Model Formulation", SPE 130702, SPE International Conference on Oilfield Scale, Aberdeen, UK, 26-27 May 2010.

Sorbie, K.S.: "A Simple Model of Precipitation Squeeze Treatments", SPE 155111, SPE International Conference on Oilfield Scale, Aberdeen, UK, 30-31 May 2012.

Sweeney, F.M. and Cooper, S.D.: "The Development of a Novel Scale Inhibitor for Severe Water Chemistries", SPE 25159, SPE International Symposium on Oilfield Chemistry, New Orleans, Los Angeles, 2-5 March 1993.

Szkatula, A., Balanda, M., and Kopec, M.: "Magnetic Treatment of Industrial Water. Silica Activation", *European Physical Journal – Applied Physics*, Vol. 18, pp. 41-49, 2002.

Tomson, M.B., Kan, A.T., Fu, G. and Al-Thubaiti, M.: "A Molecular Theory of Mineral Scale Inhibition", CORROSION 2004.

Tomson, M.B., Kan, A.T., Fu, G., Shen, D., Nasr-El-Din, H.A., Al-Saiari, H. and Al-Thubaiti, M.: "Mechanistic Understanding of Rock/Phosphonate Interactions and the Effect of Metal Ions on Inhibitor Retention", *SPE Journal*, pp. 325-336, September 2008.

Tomson, M.B., Fan, C., Lu, H., Zhang, P, Al-Saiari, H. and Kan, A.T.: "Integration of Kinetics into Scale Prediction Software, ScaleSoftPitzer", SPE International Symposium on Oilfield Chemistry, The Woodlands, Texas, USA, 20-22 April 2009.

Van der Leeden, M.C., Reediji, J. and Van Rosmalen, G.M.: "The Influence of Various Phosphonates on the Growth Rate of Barium Sulphate Crystals in Suspension", Estudios Geol., 38, p279-287, 1982.

Van der Leeden, M.C. and Van Rosmalen, G.M.: "Development of Inhibitors for Barium Sulphate Deposition", 3rd International Symposium on Chemicals in the Oil Industry, pp.65-85, 1988a.

Van der Leeden, M.C. and Van Rosmalen, G.M.: "Inhibition of Barium Sulfate Deposition by Polycarboxylates of Various Molecular Structures", SPE Production Engineering, February 1990 or SPE 17914, 1988b.

Vazquez, O., Mackay, E.J. and Sorbie, K.S.: "Development of a Non-Aqueous Scale Inhibitor Squeeze Simulator", SPE 100521, SPE International Oilfield Scale Symposium, Aberdeen, 31 May-1 June 2006. DOI: 10.2118/100521-MS.

Vazquez, O., Sorbie, K.S. and Mackay, E.J.: "A General Coupled Kinetic Adsorption/Precipitation Transport Model for Scale Inhibitor Retention in Porous Media: II Sensitivity Calculations and Field Predictions", SPE 130703, SPE International Conference on Oilfield Scale, Aberdeen, UK, 26-27 May 2010.

Vetter, O.J.: “The Chemical Squeeze Process – Some New Information on Some Old Misconceptions”, Journal of Petroleum Technology, pp.339-353, March 1973.

Vetter O.J.: “Oilfield Scale - Can we handle it?”, Journal of Petroleum Technology, pp.1402-1406, December 1976.

Vu, V.K., Hurtevent, C. and Davis, R.A.: “Eliminating the Need for Scale Inhibition Treatments for Elf Exploration Angola’s Girassol Field, SPE 60220, 2nd SPE International Symposium on Oilfield Scale, Aberdeen, UK, 26-27 January 2000.

Wang, Z., Neville, A. and Meredith, A.W.: “How and Why Does Scale Stick – Can the Surface Be Engineered To Decrease Scale Formation and Adhesion?” SPE 94993, SPE International Symposium on Oilfield Scale, Aberdeen, UK, 11-12 May 2005.

Wat, R., Montgomerie, H. Hagen, T, Boreng, Raymond, Kotlar, H.K. and Vikane, O.: “Development of an Oil-Soluble Scale Inhibitor for a Subsea Satellite Field”, SPE 50706, International Symposium on Oilfield Chemistry, Houston, Texas, 16-19 February 1999.

Weatherford ClearWELL 2009-2010:
http://www.weatherford.com/ECMWEB/groups/web/documents/weatherfordcorp/WFT100054.pdf

Weintritt D.J. and Cowan, J.C.: “Unique Characteristics of Barium Sulphate Scale Deposition”, Journal of Petroleum Technology, pp.1381-1394, 240, October 1967.

Williams, G., MacDonald, A., Wylde, J., Shields, C, Smitton, C., Frampton, H., Morgan, J. and Morris, A.: “Late-Life Production Boost for BP Miller With Combined Scale Squeeze and Chemical Water-Shutoff Treatment”, SPE 100660, International Oilfield Scale Symposium, Aberdeen, Scotland, UK, 30 May-1 June 2006.

Wilson, D.: “Influence of Molecular Weight on Selection and Application of Polymeric Scale Inhibitors”, Paper no. 48, NACE Annual Conference, Baltimore, Maryland, 28 February-4 March 1994.

Wylde, J.J., Allen, G.C. and Collins, I.R.: “A Novel Surface Sensitive Approach to Quantitatively Measuring the Prediction and Inhibition of Scale Growth”, SPE 68299, SPE 3rd International Symposium on Oilfield Scale, Aberdeen, UK, 30-31 January 2001.

Yuan, M.D., Sorbie, K.S., Todd, A.C., Atkinson, L.M., Riley, H and Gurden, S.: "The Modelling of Adsorption and Precipitation Scale Inhibitor Squeeze Treatments", SPE 25163, SPE International Symposium on Oilfield Chemistry, New Orleans, LA, 3-5 March 1993.

Yuan, M.D., Todd, A.C. and Sorbie, K.S.: "Sulphate Scale Precipitation Arising from Seawater Injection – A Study with Aid of a PC-Compatible Prediction Model", Chemistry and Origins of North Sea Formation Waters Meeting, London, 15 January 1994.

Yuan, M.D.: "Water Scaling in North Sea Oil Fields and Scale Prediction – An Overview", NIF 7th International Symposium on Oilfield Chemicals, Geilo, Norway, 1996.

Yuan, M.D., Jamieson, E. and Hammonds, P.: "Investigation of Scaling and Inhibition Mechanisms and the Influencing Factors in Static and Dynamic Inhibition Tests" Paper 98067, NACE Annual Conference and Exposition Corrosion 98, San Diego, California, 22-27 March 1998.

Yuan, M.D.: Barium Sulfate Scale Inhibition in Deepwater Cold Temperature Environment, SPE 68311, 3rd International Symposium on Oilfield Scale, Aberdeen, UK, 30-31 January 2001.

Zhang, H.R. and Sorbie, K.S.: "SQUEEZE Software", Department of Petroleum Engineering, Heriot Watt University, Edinburgh, 1997.

Zhang, H., Mackay, E.J., Chen, P. and Sorbie, K.S.: "Non-Equilibrium Adsorption and Precipitation of Scale Inhibitors: Corefloods and Mathematical Modelling", SPE 64755, SPE International Oil and Gas Conference and Exhibition, Beijing, China, 7-10 November, 2000. DOI: 10.2118/64755-MS.

Zhang, N., Kan, A.T., Shi, W., Al-Saiari, H. and Tomson, M. B.: "A Novel Approach to the Study of $CaCO_3$ Precipitation Kinetics on Carbon Steel Pipe", SPE 155263, SPE International Conference and Exhibition on Oilfield Scale, Aberdeen, UK, 30-31 May 2012.

# Appendix A Experimental Procedures

**Note: The author either developed or was very closely involved in the training and development of the experimental procedures in all of the papers submitted. Details of these developed test procedures are given in this Appendix.**

## A.1 Paper 1

Graham, G.M., Boak, L.S. and Sorbie, K.S.: "The Influence of Formation Calcium and Magnesium on the Effectiveness of Generically Different Barium Sulphate Oilfield Scale Inhibitors", *SPE Production and Facilities*, Vol. 18, Issue No. 1, pp.28 - 44, February 2003.

### A.1.1 General Static Inhibition Efficiency Test Procedure: "Acetate" Buffered

In these tests each individual test condition is conducted in duplicate to allow anomalous results, to be immediately recognised. Tests would be repeated if the difference in the recorded efficiencies was > 5 – 10%. The experimental procedure for the acetate buffered static barium sulphate inhibition efficiency tests is described in detail below (FW = Formation Water, SW = Sea Water):

1. Prepare the two brines (FW containing $Ca^{2+}$, $Ba^{2+}$ etc. and SW containing $SO_4^{2-}$, $HCO^{3-}$ etc.), depending on which brine you require, by dissolving the appropriate salts in distilled water, as shown in Table A1.1.

| Table A1.1 | Brine composition used in this study | | | | |
|---|---|---|---|---|---|
| | | | | | |
| **Effect of calcium at constant magnesium concentration** | | | | Brine compositions after mixing | |
| Ion | Brent Type | Forties Type | Sea Water | 50:50 SW:Brent FW | 60:40 SW:Forties FW |
| Sodium | 9000 | 31275 | 10890 | 9945 | 19044 |
| Potassium | 200 | 654 | 460 | 330 | 538 |
| Magnesium | 50 | 739 | 1368 | 709 | 1116 |
| Barium | 80 | 269 | 0 | 40 | 108 |
| Strontium | 60 | 771 | 0 | 30 | 308 |
| Sulphate | 0 | 0 | 2960* | 1480 | 1776 |
| Chloride | 14300 | 60412 | 19766 | 17033 | 36024 |
| | | | | | |
| Calcium (i) | 0 | 0 | 428 | 214 | 257 |
| Calcium (ii) | 250 | 1000 | 428 | 339 | 657 |
| Calcium (iii) | 1000 | 2000** | 428 | 714 | 1057 |
| Calcium (iv) | 2000 | 5000 | 428 | 1214 | 2257 |
| | | | | | |
| Notes: | | | | | |
| * 0ppm sulphate SW used for compatibility studies | | | | | |
| ** 2000ppm calcium Forties FW used in "Mechanisms of Interaction studies | | | | | |
| | | | | | |
| **Effect of magnesium at constant calcium concentration** | | | | Brine compositions after mixing | |
| Ion | Brent Type | Forties Type | Sea Water | 50:50 SW:Brent FW | 60:40 SW:Forties FW |
| Sodium | 9000 | 31275 | 10890 | 9945 | 19044 |
| Potassium | 200 | 654 | 460 | 330 | 538 |
| Calcium | 0, 1500 | 0, 2643 | 0 | 0, 750 | 0, 1057 |
| Barium | 80 | 269 | 0 | 40 | 108 |
| Strontium | 60 | 771 | 0 | 30 | 308 |
| Sulphate | 0 | 0 | 2960 | 1480 | 1776 |
| Chloride | 14300 | 60412 | 19766 | 17033 | 36024 |
| | | | | | |
| Magnesium (i) | 0 | 0 | 0, 0 | 0 | 0 |
| Magnesium (ii) | 0 | 0 | 500, 600 | 250 | 360 |
| Magnesium (iii) | 0 | 0 | 1418, 1368 | 709 | 821 |
| Magnesium (iv) | 0 | 0 | 2000, 1860 | 1000 | 1116 |

Table A1.1: Various Brine Compositions used in this Study

2. Vacuum filter brines separately through 0.45µm membrane filter paper.
3. Dissolve the inhibitor in the sea water brine to create a stock solution of 1,000 ppm active SI.
4. The inhibitor solution is then further diluted in SW to give the required concentration for the particular test. Each inhibitor concentration is tested in duplicate (therefore 2 x SI/SW volume is prepared)

**Note:** the concentration of inhibitor in the sea water must be higher than that required for the test by a factor which accounts for the dilution when mixed with the formation water.

5. Measure out appropriate volumes of FW and SW/SI into their separate "Azlon" (polyethylene) bottles. For example, for a 50:50 mix, measure out 100ml SI/SW and 100ml of FW for each test.
6. Add 2 ml (1 ml buffer/100 ml final brine mixture) of buffer solution* to the SI/SW solutions, taking extreme care not to introduce impurities and cap all bottles securely. Shake the bottles to ensure full mixing of buffer with SI/SW solution.

   **Note:** The buffer is added to the SW solution to ensure that if the SW brine was self-scaling at the test pH, then the SI prevents precipitation occurring until it is mixed with the FW. Also, any precipitation formed prior to mixing, could induce further precipitation on contact with FW, creating false results.
7. Place the bottles containing the SI/SW/buffer into a waterbath and the bottles containing the FW into an oven, both set to the required temperature, for tests of a 50:50 mixing ratio. Leave for ~60 minutes to reach test temperature.

   **Note:** For a test using a different mixing ratio (e.g. 10:90), place the bottles with the larger volume (90%, 180ml) into the oven, and the bottles of smaller volume (10%, 20ml) into the waterbath.
8. After 60 minutes, mix the two brines together. For a 50:50 mixing ratio, add the FW to the SI/SW/buffer solution and shake quickly, ensuring maximum mixing is achieved (for worst case scenario). For different mixing ratios, always add larger volume to smaller volume, and shake again. Start a stopclock (t = 0).

   **Note:** The water bath should have sufficient polystyrene balls on the surface to keep evaporation to a minimum.
9. The tests are then sampled at the required time, typically t = 2 and 22 hours, as described below.
10. In certain experiments, the pH values can be carefully monitored at the test temperature and again on cooling, after the tests. In all cases, record the initial and final pH values.

* The acetic acid/sodium acetate buffer solution is prepared in order to give the required pH. For example in order to obtain a pH of approximately 5.5, the buffer solution is prepared by dissolving the following amounts of Analar grade reagents into 100 ml of distilled water:

13.60g sodium acetate tri-hydrate + 0.5g acetic acid

**Note:** The actual pH obtained must be checked prior to testing: For example, for a 50:50% mix, add 1ml of buffer to 100ml FW, and 1ml of buffer to 100ml SW. Record the individual pH values. Add the FW to the SW and record the pH, checking it is of appropriate value, ~pH5.5.

**Sampling and Analysis**

The sampling procedure adopted depends on the severity of the particular scaling system being studied. The procedure below is used for a medium scaling brine system such as a 50:50 mixture of a Forties type formation water ($[Ba^{2+}]$ = 269ppm) and sea water ($[SO_4^{2-}]$ = 2,960ppm). Modified sampling procedures for low scaling and high scaling brine mixtures are given below.

The sampling procedure is carried out as follows: The stabilising/dilution solution contains 1,000 ppm commercial polyvinyl sulphonate scale inhibitor* (PVS) and 3,000 ppm potassium (as KCl) in distilled water, adjusted to pH 8 – 8.5. The solution of 1,000 ppm PVS has been shown to effectively stabilise (or quench) the sample and thus prevent further precipitation. The potassium is included in this solution to act as an ionisation suppressant for the Atomic Absorption determination of barium. The standard analytical approach currently used within FAST laboratories for barium, is Inductively Coupled Plasma (ICP) Spectroscopy. 9ml of this potassium/PVS solution is added to a test-tube at room temperature using an Eppendorf 10ml automatic pipette. After the required time interval, 1ml of the particular test supernatant waters is removed using an Eppendorf 1ml pipette and immediately added to the 9ml of potassium/PVS solution. The samples are then analysed by ICP for the particular ions of interest, e.g. barium, strontium, calcium, magnesium. For strontium, calcium and magnesium, additional dilutions will be required.

* **Note:** a polycarboxylate scale inhibitor was initially used in the quenching solution. However, more recent tests using very high salinity formation brines resulted in precipitation of a polycarboxylate/divalent cation complex following sampling.

The required efficiencies for $BaSO_4$ ($SrSO_4$, $CaSO_4$ or $MgSO_4$) inhibition is then calculated using the following, Equation (10):

$$\text{Inhibition Efficiency (IE), \%} = 100 \times \frac{(C_I - C_B)}{(C_O - C_B)} \qquad (10)$$

where; $C_I$ = concentration of barium at sampling time

$C_B$ = concentration of barium in the blank solution (no inhibitor)

$C_O$ = concentration of barium originally in solution (i.e. at time = 0).

**Note:** $C_0$ is determined by adding the test FW and SW to the KCl/PVS quenching solution, in the appropriate ratio as for the quenched test solutions. $C_0$ samples are added to the ICP analysis of test samples at regular intervals to allow for instrumental errors to be accounted for.

***Sampling Time:*** Samples are typically taken and analysed at t = 2 hours and 22 hours. Monitoring at t = 2 and 22 hours allows for the *mode* of the inhibition mechanism to be examined - early time would broadly represent the *nucleation period/growth retardation* mechanism and the later time would be the *crystal growth blocking* mechanism. 2 hours represents an appropriate time duration between the initial mixing of the brines in the near wellbore area and the time taken for the fluids to reach production facilities under normal operating conditions. 22 hours is a much longer residence time than inhibitor products would normally be required to be effective. Note that in various specialised studies we sometimes take more sampling times, as early as ~0.25 hours (about the earliest time an analysis can be done) and as long as 200+ hours in our low sulphate kinetic deposition studies.

**Modified Sampling Procedures**

***Low scaling waters:*** For waters with a low scaling tendency and a relatively low concentration of barium in the initial mixed brine, (for example 50:50 mixes of formation water/sea water containing less than 100ppm barium initially upon mixing) the sampling procedure can be altered as follows:

4ml of sample is added to a test-tube containing 4ml of the KCl/PVS solution described above.

This lower dilution allows for greater accuracy in the determination of barium by ICP.

***High scaling waters:*** For particularly severe water mixtures the sampling procedure has to be further modified. For example, a 50:50 mixture of South Brae FW and SW has a supersaturation in excess of 50 at 95°C, with almost 1,000ppm barium initially present. In such cases, the sampling strategy described above is not completely effective at stabilising further precipitation prior to analysis. The sampling strategy is thus altered to that described below:

1ml of sample is added to a test-tube containing 19ml of the KCl/PVS solution described above.

***Low Scaling (Brent Type FW) Brine Efficiency Tests***

1. The buffer solution used in this work was prepared freshly each week by dissolving 13.60g sodium acetate tri-hydrate + 0.5g acetic acid in distilled water and making up to the mark in a 100ml volumetric flask. This was to give a mix pH value of 5.2.
2. Tests temperature: 95$^{o}$C
3. The brine mixture examined was the highest supersaturation for this mix; i.e. 50:50 SW/Brent type FW.
4. Various calcium and magnesium concentrations were introduced into the formation water brine in order to examine a variety of mixed brine cation concentrations.
5. Inhibitors examined included penta-phosphonate (DETPMP), phosphino-polycarboxylate (PPCA), and poly vinyl sulphonate (PVS).
6. Inhibitor concentration level of 2ppm active was used for all of the inhibitor types.
7. The mixed brine solutions were then sampled at the required time intervals in the following manner: 6ml of an aqueous solution containing 3000ppm of potassium (as KCl) and 1000ppm of PPCA inhibitor (adjusted to a pH value of 8) was added to a test tube at room temperature – the quench solution. 4ml of the particular test supernatant solution was removed using an automatic Eppendorf 10ml pipette and immediately added to the 6ml of stabilisation/diluent solution.

***Medium Scaling (Forties Type FW) Brine Efficiency Tests***

1. The experimental procedure for these tests is similar to that described above except for the sampling stage.
2. The test pH was controlled using the buffer solution to a pH value of ~ 6.0. This was done to ensure similar extents of dissociation of the different functional groupings present in the generically different species under examination. The buffer solution used was prepared freshly each week by dissolving 13.60g sodium acetate tri-hydrate + 0.038g acetic acid in distilled water and making up to the mark in a 100ml volumetric flask.
3. All tests were performed at 95˚C.
4. The scaling mixture examined was the highest supersaturation mixture for this brine system; i.e. 60:40 SW/Forties type FW.
5. Various calcium and magnesium concentrations were introduced into the formation water brine in order to examine a variety of mixed brine cation concentrations.
6. Inhibitors examined included penta-phosphonate (DETPMP), hexa-phosphonate (Hexa-P), phosphino-polycarboxylate (PPCA), poly vinyl sulphonate (PVS) and sulphonated-polyacrylate (VS-Co).
7. Inhibitor concentration of 8ppm active was used for all of the inhibitor types. The higher level used in these tests (cf. 2ppm above) simply reflects the fact that this is a higher scaling tendency brine mixture.
8. Sampling: 1ml of supernatant and quenching into 9ml of the KCl/PPCA quench solution described above.

***Medium Scaling (Forties Type FW) Brine Compatibility Tests***

1. Tests performed to examine inhibitor compatibility with increasing calcium concentration in this mixed brine system.
2. Inhibitors examined were PPCA and DETPMP.
3. The same calcium concentrations which were used previously in the inhibition efficiency tests for the medium scaling brine system were investigated here. The only difference in the mixed solutions was that sulphate-free seawater was introduced rather than seawater. This change to sulphate-free seawater was done in order to exclude barium sulphate dropout in these tests, so that only the issue of compatibility was being investigated.

4. Two different brines, namely synthetic sulphate-free sea water (SFSW) and the medium scaling Forties type FW.
5. Mixing ratio examined was 60:40 SFSW:FW as used in the efficiency testing.
6. Inhibitors diluted to 0, 8, 50, 100 and 500ppm active.
7. 100ml of each solution was buffered to pH6 before being placed in an oven and raised in temperature stepwise to 95˚C and left to equilibrate over 2 hours.
8. After equilibration at 95˚C, the solutions were filtered through 0.22 μm filter paper at the test temperature of 95˚C.
9. Each of the filter papers was left to dry prior to SEM/EPM study (see below).
10. For the PPCA and DETPMP samples, the residual inhibitor was analysed by ICP.

***Scanning Electron Microscopy and Electron Microprobe Microscopy***

1. The compositions of both the PPCA and DETPMP precipitates which were formed in the 500ppm active inhibitor compatibility experiments described above for the medium scaling (Forties type) brine were further examined by SEM and EPM techniques.
2. SEM images show the size and morphology of the particles which make up the precipitate.
3. EPM then provides elemental analysis of the precipitate sample.
4. The filter papers retained from the previous compatibility tests were allowed to dry.
5. A sample of precipitate was then scraped off the filter paper on to an SEM stub which was then ready for analysis by SEM.

***Mechanism of Interaction - Comparative Inhibitor Adsorption***

1. Tests conducted in a similar manner to the previous inhibition efficiency tests on the medium scaling tendency (Forties type) brine mixture.
2. Residence times examined for both the efficiency and inhibitor concentration monitoring were 0.5, 1, 2, 4 and 22 hours.
3. Both sets of tests were performed at one calcium concentration only, 1057ppm after mixing, which was shown to be compatible in the tests described above.
4. The same water composition and 60:40 mix for both the SW and FW were used.
5. The solutions in these tests were buffered at a pH value of 5.2.
6. Five bottles for each inhibitor plus two seawater blanks underwent heating at 95˚C for 22 hours.

7. At each time interval, one of each of the inhibitor bottles was opened and analysed for both barium and inhibitor. This bottle was then discarded and a new bottle for each inhibitor was examined at the next sampling time. The experiments were performed in this manner so that the water levels within each of the tests remained the same before sampling.
8. For monitoring the inhibitor concentration, a new quenching solution had to be tested since the PPCA content in the usual solution would have contaminated the analysis results. The quenching solution used was 3000ppm potassium as KCl containing 1000ppm PVS in distilled water.
9. The sampling was conducted such that a 25ml sample was quenched in 25ml of the new KCl/PVS stabilising solution.
10. Inhibitors examined included penta-phosphonate (DETPMP), phosphino-polycarboxylate (PPCA) and a hexa-phosphonate (Hexa-P).
11. Inhibitor concentration of 8ppm active was used to compare the behaviour of the PPCA and the DETPMP. However, due to the lower threshold limit of the hexa-phosphonate, an inhibitor concentration of 3ppm active was used.

## A.2 Paper 2

Graham, A.L., Boak, L.S., Neville, A. and Sorbie, K.S.: "How Minimum Inhibitor Concentration (MIC) and Sub-MIC Concentrations Affect Bulk Precipitation and Surface Scaling Rates", *SPE Production and Operations*, Vol. 21, Issue No. 1, pp.19-25, February 2006.

### A.2.1 General Static Inhibition Efficiency Test Procedure Including a Surface

Again in these tests each individual test condition is conducted in duplicate to allow anomalous results to be immediately recognised. Tests would be repeated if the difference in the recorded results was > 5 – 10%.

The experimental equipment used in the surface growth studies is shown in Figure A2.1.

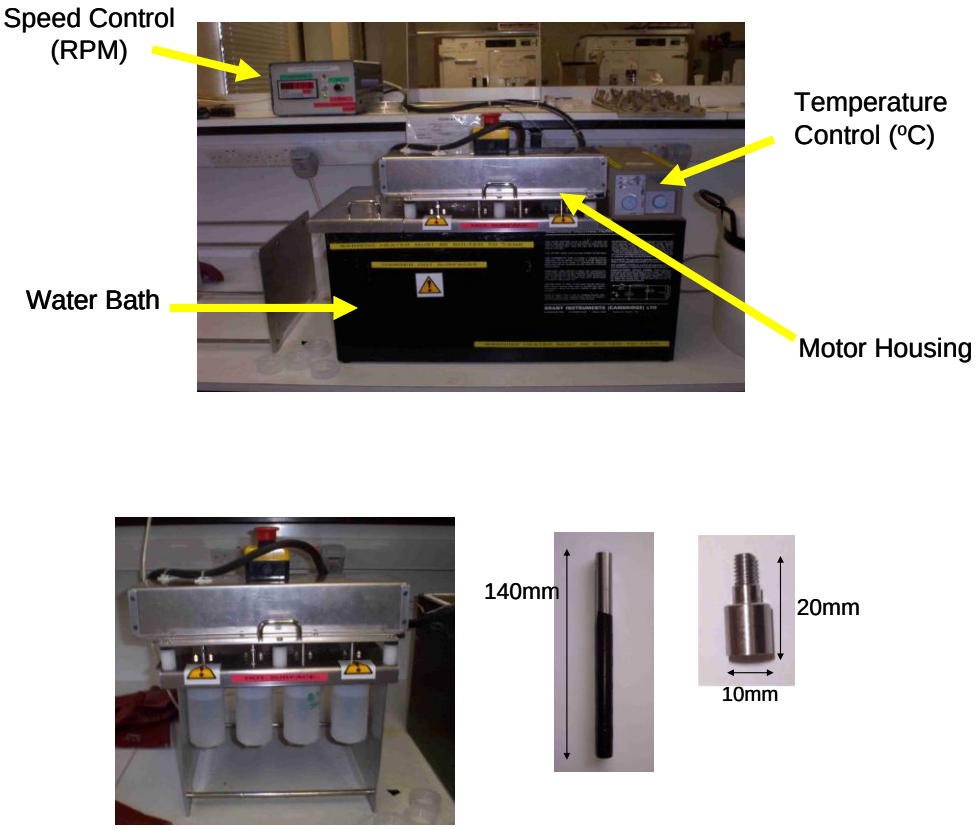



Figure A2.1: The experimental equipment used in the surface growth studies

This comprised a single-face stirrer with a motor driving four stirring rods simultaneously; a speed control unit; and a water bath with temperature control. The

metal coupons were mirror polished (6μm) and cleaned with isopropyl alcohol (IPA) and distilled water (DW) prior to use. The coupon and mounting rod were then covered with insulating tape so that only the mirror-polished surface was exposed to the brine. The coupons were rotated at a speed of 600rpm (Reynolds number, Re ≈ 1378) giving laminar flow conditions.

**Materials and conditions:**

1a. ***Brines*.** Forties Type Formation Water (FW) and Seawater (SW) as detailed in Table A2.1.

| COMPOSITION OF THE BRINES USED IN THIS STUDY | | | | |
|---|---|---|---|---|
| | Forties type FW | | SSW | |
| Ion | (ppm) | g/l | (ppm) | g/l |
| Na | 31,275 | 79.5 | 10,890 | 24.41 |
| Ca | 2,000 | 10.93 | 428 | 2.34 |
| Mg | 739 | 6.18 | 1,368 | 11.44 |
| K | 654 | 1.25 | 460 | 0.877 |
| Ba | 269 | 0.48 | – | – |
| Sr | 771 | 2.35 | – | – |
| $SO_4$ | 0 | – | 2,690 | 3.98 |
| Cl | 55,279 | – | 19,972 | – |

Table A2.1: Composition of the Brines Used in This Study

b. Examined at a mixing ratio of 10:90 seawater (SW): Forties type formation water (FW). The brines were filtered through a 0.45-μm filter paper before use.

c. The initial values of supersaturation ratio were calculated to be approximately, *Sp* = 800, 190, and 80 at 5, 50, and 95°C, respectively. These were determined using the Multiscale prediction software (Petrotech 1998).

***Scale Inhibitor, SI Solution*.** A 1,000ppm active solution of PPCA was prepared in filtered SW and subsequent dilutions were made to prepare the working standards, as detailed in Table A2.2.

| RANGE OF PPCA CONCENTRATIONS (ACTIVE) USED IN BULK JAR AND SURFACE-GROWTH TESTS | | |
|---|---|---|
| | Range of [PPCA] (ppm) tested | |
| Temperature (°C) | Bulk Jar Tests | Surface-Growth Tests |
| 5 | 2, 2.5, 3, 3.5, 4 | 1.5, 2, 2.5, 3, 3.5, 4, 6, 8,10 |
| 50 | As for 5°C | 1.5, 2, 2.5, 3, 3.5, 4 |
| 95 | 3, 4, 6, 8, 10 | As for 5°C |

Table A2.2: Range of PPCA concentrations (active) used in bulk jar and surface growth tests

2. ***Buffer Solution.*** Acetate buffer was prepared by dissolving 34g sodium acetate trihydrate in ~240ml distilled water (DW). To this, 1.02g of glacial acetic acid was added and the volume was made up to 250ml. This gave a pH of 5.47 when 2ml was added to 200ml of a 10:90 SW:FW mix.
3. ***Quenching Solution.*** This solution was prepared by dissolving 28.55g of potassium chloride in ~4.8L DW. To this, 5g of polyvinylsulphonate (PVS) dissolved in ~20ml distilled water was added. The pH was then adjusted to between 8 and 8.5, and the volume was made up to 5L.
4. ***Dissolver Solution.*** This solution was prepared by dissolving 12.5g of diethylene-triamine-penta acetic acid (DTPA) and 12.5g of potassium hydroxide (KOH) in 250ml DW, giving a pH of approximately 12.

**General Procedure:**

1. 180ml of FW was measured into a new HDPE test bottle at room temperature.
2. 2ml of freshly prepared buffer solution was then added to the same test bottle.
3. 20ml of SW was measured into a new HDPE test bottle at room temperature.
4. Both SW and FW samples were heated in the water bath or oven at the test temperature for 1 hour.
5. The SW was then added to the FW but not shaken. The following procedures were then undertaken immediately:

***Bulk Jar Tests*.** The bottles were capped and then placed in the water bath in triplicate sets for each concentration.

***Surface-Growth Studies.*** The bottles were mounted onto the stirrer unit with the coupons and mounting rods in place and the stir speed set to 600rpm.

**Sampling and Analysis:**

6a. ***Bulk Inhibition.*** At each sampling time, 1ml of test supernatant was withdrawn and diluted in 19ml of quenching solution before analysis for [$Ba^{2+}$] by Inductively Coupled Plasma, ICP.

6b. ***Quantitative Analysis of Surface Coverage.*** Coupons from each test were removed from the supernatant and rinsed lightly with DW. The coupon was placed in 10ml DTPA-KOH solution (in a stoppered test tube) for 48hours to dissolve the surface precipitate. The amount of surface precipitate was then quantified by analyzing the amount of dissolved $Ba^{2+}$ by ICP. Results are presented as mg of $Ba^{2+}$.

6c. ***Determination of Residual [SI] in Bulk Solution.*** A further 25ml of supernatant was removed from each bottle, diluted in 25ml quenching solution and analyzed for [SI] using the Hyamine 1622 method (Graham et al. 1995). A modified concentration step (refer to A.2.2) was used because of the low [SI], whereby the standard 10ml volumes of sodium citrate solution, DW, and Hyamine 1622 used in the final steps were reduced to 3ml, and the final volume of solution was made up to 10ml.

### A.2.2 Hyamine PPCA Concentration Step for Surface Growth Studies

This method is to monitor low PPCA concentrations in surface nucleation and growth tests over varying residence times. The diluting solution for the calibration standards is the same mixing ratio and sampling regime used in the bottle tests. For example, if the bottle tests were performed at a 10:90 mix of SW:FW and then sampled for scale inhibitor analysis by taking 25ml test sample into 25ml KCl/PVS to quench the reaction then the diluting solution would be a 50:50 mix of 10:90 SFSW:FW to KCl/PVS.

Experimental procedure:

1. Prepare 5000ppm Hyamine 1622 (5g/l), 5% sodium citrate (56.96g/l) and KCl/PVS quenching (28.55g/5l KCl and 5g/5l PVS – adjust to between pH8.0 and 8.5 with NaOH) solutions in DW.

2. Prepare 10 x C18 Sep pak cartridges. A maximum of 10 tests can be carried out at any one time. Preparation: Push through dropwise 5ml methanol and then 10ml DW, with the long end of the C18 attached to the syringe.
3. Dilute the calibration standards from a 100ppm active inhibitor stock into plastic cups. The calibration range is 0, 0.1, 0.2, 0.3, 0.4, 0.5, 1, 2, 3, 4ppm active. The calibration can go higher but maybe limited by the top absorbance number allowed by the UV spectrometer being used i.e. absorbance units < 2.
4. Add 15 drops of the 10% HCl so that the standards are ~pH2. Test with pH paper.
5. Remove plungers of syringes. Put the prepared C18 cartridges onto 60ml syringes. Pour the first standard into the 60ml syringe, rinse cup with DW and put washings into syringe, push in plunger slightly until sealed and then turn syringe up. Remove C18 from end and expel air. Replace C18 on end. Place on Razel syringe pumps. Repeat for other calibration standards. Set syringe pumps going. Collect fluid in cup.
6. Push through remaining solution in syringes in pump set up. Throw collected fluid away as Inhibitor should be collected on C18 cartridge. Remove syringes from machine. Take off each C18 (ensure it is labelled with the std conc.) and place long end onto end of 10ml syringes filled with 10ml DW. Place on machine and set pumps going. Collect fluid in cup. Push through remaining solution in syringes in pump set up. Throw collected fluid away.
7. Take off each C18 and place short end onto end of 10ml syringes filled with 3ml 5% sodium citrate. Line up 10 x 10ml labelled volumetric flasks. Place syringes on machine and set pumps going. Inhibitor is now being taken off the C18 cartridges. Collect fluid in the separate volumetric flasks. Push through remaining solution in syringes in pump set up.
8. Take off each C18 and place short end onto end of 10ml syringes filled with 3ml DW. Place syringes on machine and set pumps going. Collect fluid in the respective separate volumetric flasks for each standard. Push through remaining solution in syringes in pump set up.
9. Put lids on flasks and take them to UV spectrometer.
10. Add 3ml 5000ppm Hyamine to flask 1 (containing 0ppm PPCA standard) with 10ml pipette and make up to 10ml with DW. Start stopclock and shake flask. After 1 minute, add Hyamine to flask 2 and follow make up procedure. Repeat with remaining flasks.

11. After 40minutes, analyse first solution in UV at 500nm and record absorbance value. Repeat at 1minute intervals for the other flasks.
12. Construct a calibration graph from the recorded standard solution absorbance values with absorbance on x-axis and SI concentration on y-axis. It is normally a 3$^{rd}$ order graph.
13. Perform repeat analysis at known concentrations i.e. 0.5 and 2ppm active PPCA to determine the repeatability of the method using the previously constructed calibration graph.
14. Repeat the procedure for samples and determine the concentration of chemical in the solution using their recorded absorbance values and the previously constructed calibration graph.

***Important additional comments:***

In steps 7 & 8, if the flasks are too small in height to be lined up with C18 ends then push through the 3ml 5% sodium citrate and 3ml DW by hand, directly into 10ml flask.

## A.3 Paper 3

Boak, L.S. and Sorbie, K.S.: "The Kinetics of Sulphate Deposition in Seeded and Unseeded Tests", *SPE Production and Operations*, Vol. 22, Issue No. 4, pp.442-450, November 2007.

### A.3.1 Experimental Details of Static Barite Precipitation Tests

The procedure for these (uninhibited) tests is detailed below:

1. Prepare 20 litres of Base Case SW and FW (no $SO_4^{2-}$ or $Ba^{2+}$ included), as detailed in Table A3.1.

| Constituents | Formation water (mg/l) | Seawater, (mg/l) |
|---|---|---|
| **Sodium** | 26,535 | 10,900 |
| **Potassium** | 1,906 | 380 |
| **Calcium** | 2,033 | 405 |
| **Magnesium** | 547 | 1,300 |
| **Barium** | 80 | 0 |
| **Strontium** | 417 | 0 |
| **Chloride** | 48,700 | 19,800 |
| **Sulphate** | 0 | 2,780 |

Table A3.1: Composition of Base Case Seawater and Formation Water (No $SO_4^{2-}$ or $Ba^{2+}$ included)

2. Using Base Case SW, dilute the amount of sodium sulphate to be dissolved to make a SW solution of 2780ppm (8.22g/2l). Repeat for all other Sodium Sulphate concentrations.
3. Repeat the process for Barium Chloride to make various FW's.
4. Prepare the buffer, ensuring that the 50:50 mixed solution of Base Case SW: Base Case FW gives a mixed pH of 6.6. Buffer; 34g Sodium acetate 3-hydrate and 0.05g of acetic acid in 250ml DW.
5. Ensure sufficient KCl/S40 for quenching the tests (Preparation; 5g S40 and 28.55g KCl in 4.8 litres and then adjust to a pH value between 8 - 8.5 before making up to 5 litres). The normal KCl/PVS quenching cannot be used as it contains sulphur ions. This will interfere with the ICP analysis that will be quantifying the concentration of $Ba^{2+}$ and $S^{-}$ left in the test solutions after each of the residence

times.

6. Depending on $Ba^{2+}$ and $SO_4^{2-}$ concentrations, the quenching dilutions for the tests were either x2 or x10 to allow accurate analysis for both $Ba^{2+}$ and $S^{-}$. Some tests required both x2 and x10 dilutions.
7. Filter each of the FW and SW.
8. Measure out 2x100ml of each FW and SW. Put the FW into 150ml bottles and then the SW is put into the 250ml test bottle. Add 2ml of buffer to each of the SW solutions and put these bottles into the waterbath at $63^{o}C$ to warm up to temperature for an hour. Place the FW bottles in the oven at $63^{o}C$ for an hour.
9. After an hour, add the FW to the SW, cap and shake the bottle and then return it to the water bath.
10. One hour after mixing, for a x2 dilution - take a 5ml sample from the test bottle and pipette it into a test-tube containing 5 ml of the quenching solution. For a x10 dilution – take a 1ml sample from the test bottle and pipette it into a test-tube containing 9ml of the quenching solution.
11. Repeat the quenching process outlined in step 10 after residence times of 2 and 22 hours after mixing. For the lowest $[Ba^{2+}]$ = 45 and 80ppm, some tests were also sampled after residence times of 48, 72, 120 and 213 hours.
12. All the quenched test solutions are now ready for ICP analysis of the remaining barium and sulphur concentrations (and strontium).
13. A control sample is run alongside the test samples of the ICP. The control sample simulates the mixing (50:50%) and quenching regime that the test samples have under gone. A control will have to be made for each of the different SW and FW mixes.

For a x2 dilution control; 5ml of SW X, 5ml of FW X are quenched into 10ml KCl/S40.
For a x10 dilution control; 1ml of SW X, 1ml of FW X are quenched into 18ml KCl/S40.

***Test Procedure - Seeded Solutions***

The seeded kinetic experiments were also performed using our previous procedure however seed crystals were introduced in an additional step, 8a as follows:

8a. Weigh out the required amount of sand particles/$BaSO_4$ seeds e.g. the no. of bottles x 0.028g.

From MultiScale (Petrotech a.s. Knowledge 1998) predictions, for a 50/50 mix of the waters, the maximum amounts of precipitate are in the range 70.13mg/l for 80 Ba 210 $SO_4$ to 44.64mg/l for 300 Ba 36 $SO_4$. Normally, the amount of seeds added is doubled to ensure that there is a large enough surface area for the reaction to be influenced by the seeds. Hence 70mg/l, divided by 5 = 14mg/200ml (test volume) x 2 mass =28mg/200ml to be added to tests (0.028g/200ml). Before being weighed out, the sand/$BaSO_4$ seeds have been washed with DW several times and then the water has been allowed to evaporate off, leaving the washed and dried sand/seeds behind. These particulates are then added with the FW into the SW in step 9 as follows:

9. Add particulates along with the FW into the SW.

## A.4 Paper 4

Kahrwad, M., Sorbie, K.S. and Boak, L.S.: "Coupled Adsorption /Precipitation of Scale Inhibitors: Experimental Results and Modelling", *SPE Production and Operations*, Vol. 24, Issue No. 3, pp.481-491, August 2009, (Online 30th July 2009).

### A.4.1 Experimental Procedure for Static Adsorption Tests

1. Static adsorption experiments were performed to evaluate the adsorption for DETPMP scale inhibitor from seawater onto crushed minerals — siderite, kaolinite, chlorite, feldspar, muscovite, and sand.
2. Experiments were performed at 25 and 95°C and at pH 4 and 6.
3. Stock solutions of DETPMP scale inhibitor were prepared using synthetic seawater, as detailed in Table A4.1.

| Ions | Conc. (ppm) |
|---|---|
| $Na^+$ | 10890 |
| $Ca^{2+}$ | 428 |
| $Mg^{2+}$ | 1368 |
| $Sr^{2+}$ | 0 |
| $Ba^{2+}$ | 0 |
| $K^+$ | 460 |
| $Cl^-$ | 19766 |

Table A4.1: Seawater Composition

4. The tests were conducted by adding 10 and 20g of minerals to 80ml (0.08L) of the DETPMP scale inhibitor solution at different concentrations (i.e., 250, 500, 1000 and 2500ppm active) before being shaken and left to sit overnight.
5. After 22 to 24 hrs, the solutions were filtered through a 0.22-μm filter, and the samples were analyzed for phosphorous, calcium, magnesium, and iron by ICP after a x10 1% $Na^+$ dilution.
6. Measure the pH values of each solution.
7. The amount of DETPMP retained by minerals ($\Gamma$ in mg SI/g rock) was calculated from the difference in DETPMP scale inhibitor concentration between stock solutions and samples. Under certain conditions ($T$ = 95˚C and pH6), precipitation of $Ca^{2+}$/$Mg^{2+}$-DETPMP salts occurred as part of the adsorption/precipitation process. In such cases, we would actually be measuring an apparent adsorption, $\Gamma_{App}$, as explained.

8. Parallel precipitation experiments were performed in the absence of minerals in order to measure the solubility of the sparingly soluble Ca/Mg/SI salts.
9. The SEM/EDAX technique was used to analyze the Ca/Mg-DETPMP precipitated complex.

## A.5 Paper 5

Boak, L.S. and Sorbie, K.S.: "New Developments in the Analysis of Scale Inhibitors", *SPE Production and Operations*, Vol. 25, Issue No. 4, pp.533-544, November 2010.

### A.5.1 C18- and $NH_2$-Cartridge Hyamine

This method is based on the turbidimetric determination of the precipitation obtained by the interaction of anionic polyelectrolytes, such as $COO^-$ ions, from COOH groups, with a quaternary ammonium salt such as Hyamine 1622. This method is susceptible to interferences from dissolved ions, in particular chloride ions, a separation stage involving adsorption onto C18 or $NH_2$ (sulphonated SI products) cartridges is necessary i.e. a solid phase extraction (SPE) technique.

Both types of cartridges are single use. When using the cartridges with aqueous solutions, it is necessary to pre-wet the cartridge with a water miscible solvent such as methanol, then flush with water before use (see Figure A5.1).

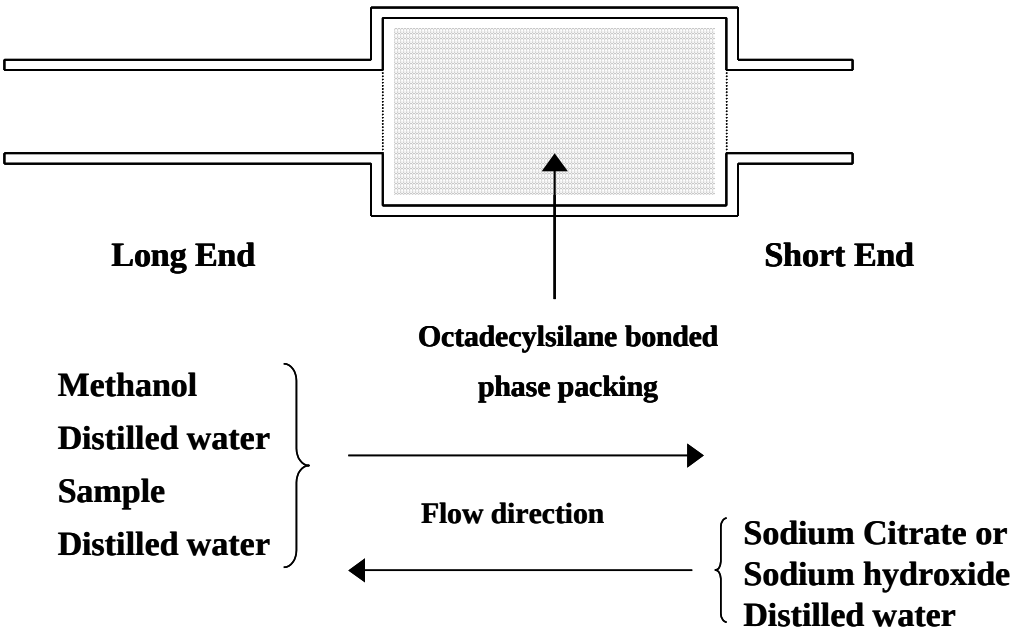



Figure A5.1: Sep-Pak C18 cartridge description

The C18 is a silica-bonded phase with strong hydrophobicity that can be used to absorb analytes of weak hydrophobicity from aqueous solutions similar to reversed-phase HPLC columns, i.e. the C18 cartridge adsorbs neutral/hydrogen bonding species strongly, but does not adsorb charged species. Thus, in order to adsorb, the inhibitor

must be in an un-charged state. To achieve this, the pH of the PPCA or MAT inhibitor solution is reduced to pH 1.5 – 2. The $pK_a$ value for a carboxylic acid grouping is ~4.5. Thus, at this low pH of 1.5 – 2, the inhibitor is effectively in the un-dissociated (uncharged) acid form. On passing through the C18 cartridge under such conditions, the inhibitor is adsorbed and effectively separated from the interfering salts, which are charged and therefore do not adsorb. The inhibitor can then be eluted from the cartridge free from the interfering salts prior to colorimetric analysis. The $NH_2$ cartridge however, although similarly silica-based, is a polar bonded phase with a basic character. This allows selectivity for acidic/basic analytes or as a weak anion exchanger in aqueous medium. It therefore works through both reverse and normal phase methodology. Having slightly different functions at retaining analytes does not affect the visible appearance of these cartridges because both types look exactly the same (Figure A5.2).

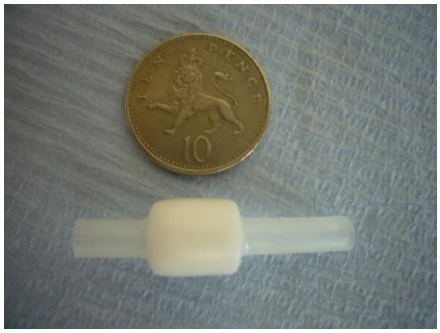


Figure A5.2: The appearance of a C18 and $NH_2$ Cartridge is exactly the same

Sample preparation time can be reduced by using Waters Sep-Pak® cartridges. These cartridges can be used to aid an analytical technique by

1. Enhancing purification of the sample by retaining the main species (i.e., SI and allowing interferences such as brine salts to flow through the system)
2. Concentrate up an SI if it is below detection level. Once the SI has been retained on the cartridge, then
3. A solvent-exchange process can be performed to allow the retained SI to be eluted into a desirable solvent for the analytical procedure that is to follow.

***C18-Cartridge Hyamine***

1. Dilute the inhibitor stock solution to make 50ml standards at concentrations of 0 to 10ppm active in the appropriate brine (i.e., SW, FW).

2. Adjust 50ml of each standard solution to pH 1.5 to 2.0 by dropwise addition of hydrochloric acid 10% v/v.
3. Attach a 5ml syringe of methanol to the long end of a Sep-Pak C18 cartridge. Pass the methanol through the cartridge dropwise and discard the expelled solution.
4. Using a syringe, pass 10ml of DW slowly through the cartridge and discard the expelled solution.
5. Using a 60ml syringe and the Razel syringe pumps, pass inhibitor solution through the cartridge (7 to 8 minutes of flow). Collect the fluid in a cup.
6. Wash the cartridge from the same end with 10ml of DW from a syringe, again using the Razel syringe pumps. The combined collected fluids from Steps 5 and 6 for each of the standard solutions can now be discarded, because the inhibitor should be adsorbed onto the cartridge.
7. Invert the cartridge and attach to the short end a syringe containing 10ml of a 5% solution of sodium citrate in DW.
8. Elute the inhibitor slowly from the C18 cartridge using the 10ml of sodium citrate solution on the syringe pumps and collect each eluent in a 50ml volumetric flask.
9. Using the same 10ml syringe, pass 10ml of DW through the C18 cartridge, again collecting the eluent in the 50ml volumetric flask.
10. Pipette 10ml of a 5,000ppm (as supplied) aqueous solution of Hyamine 1622 into the flask and dilute to the mark (50ml) with DW. A time interval of 1 minute is suggested for the addition of Hyamine to each flask to allow for analysis time on the spectrophotometer.
11. Shake the volumetric flask rapidly to ensure that the solutions are mixed, and leave to stand for 40 minutes.
12. After 40 minutes, measure the absorbance of each of the standard solutions at 500nm using a spectrophotometer.
13. Construct a calibration graph from the recorded standard solution absorbance values with absorbance on x-axis and SI concentration on y-axis. It is normally a third-order curve.
14. Perform repeat analysis at known concentrations (i.e. 0, 2 and 5ppm) to determine the method repeatability using the previously constructed calibration graph with absorbance on the x-axis and SI concentration on the y-axis.
15. Repeat the procedure for samples and determine the concentration of chemical in the solution using their recorded absorbance values and the previously constructed

calibration graph. Remember to include blanks and repeat standards within the analysis run.

***$NH_2$-Cartridge Hyamine***

The procedure for the $NH_2$-cartridge Hyamine is similar to that of the C18-cartridge procedure detailed except

1. Use $NH_2$, amino-propyl cartridges and substitute 0.1N NaOH for the 5% sodium citrate, in Steps 7 and 8.
2. Include Step 9a. Pipette 10ml of 5% sodium citrate into a 50ml flask after the NaOH and DW, but before the addition of 10ml Hyamine.

### A.5.2 OASIS® 2×4 Method

This family of extraction products - MCX, MAX, WCX, and WAX (see below for descriptions) - combine the right absorbent chemistry with robustness and sensitive/selective solid phase extraction (SPE) methods. MCX and MAX are two mixed-mode strong-ion-exchange chemistries to address weak basic and acidic compounds, respectively, while WCX and WAX selectively extract strongly basic and strongly acidic compounds, respectively. By using all four cartridges in the Oasis® 2×4 Method alongside the Oasis® hydrophilic-lipophilic-balanced (HLB) cartridge, the reversed phase sorbent, they provide a simplified strategy for method development by selecting the correct SPE sorbent and protocol.

In summary,

Oasis® HLB - hydrophilic-lipophilic-balanced reversed phase sorbent for acids, bases, and neutrals

Oasis® MCX - mixed-mode cation-exchange reversed phase sorbent for bases

Oasis® MAX - mixed-mode anion-exchange reversed phase sorbent for acids

Oasis® WCX - mixed-mode weak cation-exchange reversed phase sorbent for strong bases (e.g., quaternary amines)

Oasis® WAX - mixed-mode weak anion-exchange reversed phase sorbent for strong acids (e.g., sulfonates)

Although there are four different sorbent types and the HLB cartridge, only two protocols for detection are required. The MCX and WAX cartridges can be paired together and follow one protocol, while MAX and WCX follow another to extract acids,

bases, and neutrals with high SPE recoveries while removing matrix components that may interfere with analysis. The main advantage of this Oasis® 2×4 Method is the key features of the sorbent material. It has stability at all pH values from pH = 0 to pH > 14, allowing great flexibility for retaining the SI and in a wide range of solvents (i.e., different types of acids/alkalis), allowing significant retention of polar compounds while having a hydrophobic retention capacity that is three times that of the traditional C18. The sorbent capacity/performance is not affected by drying out as in the C18 because the sorbent is polymeric and has hydrophilic portions that "hang on" to the water in contrast to the C18/$NH_2$ silica, which actively tries to expel the water from its pores, causing a drying-out effect and loss of retention. These mixed-mode cartridges operate through both reversed phase and ion-exchange, enabling much stronger washes, resulting in very clean extracts. There is no analyte breakthrough or loss of recovery because of dissolving silica particles at high pH or cleaving the bonded phase at low pH. One major overriding advantage of the Oasis® 2×4 Method is that large batches of 20 samples can be prepared simultaneously as opposed to 10 using the C18 or $NH_2$ cartridges, making the whole process more efficient.

To address any source of pipetting error, a larger introduction vessel was attached to an adaptor that consequently fitted into the top of the previously used cartridge, as shown in Figure A5.3.

Figure A5.3: Photo of the Oasis® 2x4 Method apparatus including the larger introduction vessels, the adaptors, cartridges and a vacuum pump to draw the fluids through the system

For more information on these cartridges or the Oasis® 2×4 Method and protocols, visit www.waters.com and www.waters.com/oasis .

The Oasis® cartridges - MAX, MCX, WAX, WCX, and HLB - being used have a 3ml volume capacity and contain 60mg sorbent (higher sorbent capacity is 150mg), which has a particle size of 30µm. The main cartridge used by FAST for their analysis has been the WAX cartridge. The following procedure will be based on the WAX protocol.

1. Dilute the inhibitor stock solution (normally 100ppm active) to make 10ml standards at concentrations of 0 to 10ppm active in the appropriate brine (i.e. SW).
2. Adjust 10ml of each standard/repeat solution to pH1.5 to 2.0 by drop-wise addition of hydrochloric acid 10% v/v.
3. Set up the Oasis tank with no test-tube rack inside and the vacuum pump apparatus with waste flask in line between the tank and pump.
4. Put holders into tank top plate before attaching a cartridge to each holder. Block off any free openings not being used, although calibration and method repeats can be performed simultaneously, which potentially uses up all holders. Remember to label cartridges.
5. To the top of each cartridge, attach an adaptor and then a large introduction vessel ensuring that all the pieces are securely together to avoid leaks and loss of fluids, which would introduce errors.
6. To prepare the cartridges, pipette 5ml of methanol into each cartridge by the large introduction vessel.
7. Turn on the pump, adjust the valve on the tank so that the solution is being pulled through the cartridge in a drop-wise fashion. This should allow adequate contact time for each solution with the sorbent. After passing through the cartridge, the methanol goes to waste into the flask between the tank and pump. Watch the level in the flask and empty before the fluid level reaches the outlet.
8. Wait for the methanol to be fully through the cartridge before switching the pump off.
9. Add 5ml of 1.76% formic acid while following Steps 6 through 8.
10. Add 10ml of each standard repeat (at pH = 2) to its corresponding cartridge through its large introduction vessel while following Steps 6 through 8.
11. Add 5ml of 1.76% formic acid while following Steps 6 through 8.
12. Add 5ml of DW while following Steps 6 through 8.
13. Dry off the inside of the tank and place the test-tube rack containing labelled test tubes into the tank. Replace the tank top plate.

14. Add 3ml 10% ammonium hydroxide and allow it to be pulled through the cartridges into the test tubes. Turn off pump. Release pressure in tank using relief valve on top plate and remove test-tube rack of calibration standards/repeats.
15. Add 1ml of 5% sodium citrate solution to each standard/repeat solution.
16. Add 1ml of 5,000ppm (as supplied) Hyamine 1622 solution to each standard/repeat solution. Stopper the test tube, shake, and then leave for 40 minutes. A time interval of 1 minute is suggested for the addition of Hyamine to each test tube to allow for analysis time on the spectrophotometer.
17. After 40 minutes, measure the absorbance of each of the standard/repeat solutions at 500nm using a spectrophotometer.
18. Construct a calibration graph from the recorded standard solution absorbance values with absorbance on the x-axis and SI concentration on the y-axis. It is normally a third-order curve.
19. Calculate the concentration of the repeat tests at their known concentrations (i.e., 0, 0.5, 1, 4, and 6ppm) to determine the method repeatability using the previously constructed calibration graph.
20. Repeat the procedure for samples, and determine the concentration of chemical in the solution using their recorded absorbance values and the previously constructed calibration graph. Remember to include blanks and repeat standards within the analysis run.

In summary, the WAX protocol is in Table A5.1.

| Step | Why? | Vol. of soln. type & conc. | Process | Collecting Test-tubes |
|---|---|---|---|---|
| 1 | Cartridge preparation | 5ml Methanol | Equilibration | No |
| 2 | pH adjusting sorbent | 5ml 1.76% Formic Acid | pH treatment to allow better SI 'lock on' | No |
| 3 | SI solution | 10ml sample @ pH2 | SI onto cartridge | No |
| 4 | Ensure SI is 'locked on' | 5ml 1.76% Formic Acid | pH treatment to ensure SI is 'locked on' | No |
| 5 | Wash | 5ml DW | Clean up of salts | No |
| 6 | To release SI | 3ml 10% Ammonium Hydroxide | Elution of SI | Yes |
| 7 | Involved in analysis | 1ml 5% Sodium Citrate | / | / |
| 8 | Reagent | 1ml 5000ppm 'as supplied' Hyamine | Determination of [SI] | / |

Table A5.1: WAX protocol procedure

### A.5.3 Oil Analysis by Inductively Coupled Plasma (ICP)

Details of the ICP gas and set-up conditions for both aqueous and oil analysis are presented in Table A5.2.

| Settings on Ultima 2 | Aqueous | Oil |
|---|---|---|
| **Argon humidifier** | **Use** | **Do not use – tubing in its place** |
| **Power (Watts)** | **1250** | **1200** |
| **Pump Speed** | **20** | **20 ok for yellow tubing<br>10 for black tubing** |
| **Pl1 -> Pl2** | **15** | **15** |
| **AUX** | **0.8** | **0.8 Adjust on front of machine if required** |
| **G1 -> G2** | **0.2** | **0.3** |
| **$P_{neb}$** | **2.70** | **2.40 Adjusted by flow through metal nebuliser** |
| **$C_{ref}$** | **193.026@ 700V** | **247.856@ 400V** |
| **Global Rinse** | **X5 Y-20 Z75- 500 tray** | **Tray 4 position 1 – Oils tray 070509** |

Table A5.2: ICP Gas and Set-up Conditions for Aqueous and Oil Analysis

### A.5.4 Matrix Matched Easy Hyamine

***Suitability:*** Polymers such as PPCA, PAA, PMA, any anionic polyelectrolyte, species containing –COOH functional groups, any SI detected by the Hyamine complex.

This method tries to address the difficulties of determining low polymeric SI concentration from a restricted sample volume. The procedure for the actual detection is exactly the same as the normal Easy Hyamine where the interferences from the brine salts are diluted out through a large dilution in DW, but here they are matrix matched. Matrix matching means the effects of the chloride ion remaining in solution, on the chelating process between the Hyamine and SI, is the same within the calibration/repeat standards and the samples. The advantage of this method is that little pre-treatment of the sample, other than a series of dilutions in SW and then DW, is required. Therefore, it is a quick method to use.

The analytical procedure is therefore as follows:

1. Identify the inhibitor brine stock for the experiment – normally in NSSW or FW brine.
2. The calibration range for this method is 0-10ppm active; 0, 0.5, 1, 2, 3, 4, 5, 6, 8, 10ppm. From the stock solution, in step 1, make 3 series of brine standards that are x10, x5 and x2 higher than the calibration range of 0-10ppm, taking into account the dilution. Therefore, for a x10 dilution the brine standards will be 0-100ppm active inhibitor, x5 0-50ppm active, x2 0-20ppm active.

3. Having prepared each brine standard series, the next step is to dilute each corresponding series by its dilution with distilled water i.e. Dilute the x10 series 0-100ppm active, x10 in DW; 4500d 500s to make a sample volume of 5ml.
   x5 brine series 0-50ppm x5 in DW; 4000d 1000s
   x2 brine series 0-20ppm x2 in DW; 2500d 2500s
4. Add 1ml of 5% sodium citrate solution to each standard solution.
5. Add 1ml of 5,000ppm (as supplied) Hyamine 1622 solution to each standard solution. Stopper the test tube, shake, and then leave for 40 minutes. A time interval of 1 minute is suggested for the addition of Hyamine to each test tube to allow for analysis time on the spectrophotometer.
6. After 40 minutes, pour the solution into a 2cm cell and measure the absorbance at 500nm using a spectrophotometer.
7. Construct a calibration graph from the recorded standard solution absorbance values with absorbance on the x-axis and SI concentration on the y-axis.
8. Perform repeats at known concentrations (i.e., 2, 5, and 10ppm) to determine the method repeatability using the previously constructed calibration graph.
9. Repeat the procedure for samples and determine the concentration of chemical in the solution using their recorded absorbance values and the previously constructed calibration graph. Remember to include blanks and repeat standards within the analysis run.

The brine compositions used in these analytical studies are detailed below in Table A5.3;

| Ion | NSSW | Forties 'type' FW (Original $[Ca^{2+}]$ = 5038ppm) | Heron 'test' FW |
|---|---|---|---|
| | ppm | ppm | ppm |
| Na | 10,890 | 31,275 | 75,000 |
| Ca | 428 | 2,000 | 42,000 |
| Mg | 1,368 | 739 | 1,930 |
| K | 460 | 654 | 11,400 |
| Ba | 0 | 269 | 1,360 |
| Sr | 0 | 771 | 1,340 |
| $SO_4$ | 2,960 | 0 | 0 |
| Cl | 19,773 | 55,279 | 207,712 |

Table A5.3: A table of brine compositions used

## A.6 Paper 6

Shaw, S.S., Sorbie, K.S. and Boak, L.S.: "The Effects of Barium Sulphate Saturation Ratio, Calcium and Magnesium on the Inhibition Efficiency: I Phosphonate Scale Inhibitors", *SPE Production and Operations*, Vol. 27, Issue No. 3, pp.306-317, August 2012.

## A.7 Paper 7

Shaw, S.S., Sorbie, K.S. and Boak, L.S.: "The Effects of Barium Sulphate Saturation Ratio, Calcium and Magnesium on the Inhibition Efficiency: II Polymeric Scale Inhibitors", SPE 130374, SPE International Conference on Oilfield Scale, Aberdeen, UK, 26-27 May 2010. Accepted for peer review publication in *SPE Production and Operations*, potentially November 2012.

### A.7.1 Static $BaSO_4$ Inhibition Efficiency Tests

Papers 6 and 7 follow the same general experimental procedures and these are very similar to the 'General Static Inhibition Efficiency Test Procedure: "Acetate" Buffered tests', Medium scaling brine efficiency tests and the Mechanism of interaction' procedures outlined in A.1, Paper 1. The differences will be in the scale inhibitor products and their associated concentrations examined, the brine compositions and the different mixing ratios used. In addition, when the scale inhibitor was being measured, if ICP was not an option then wet chemical techniques such as Hyamine 1622 and the Pinacyanol chloride blue dye method were performed.

The volume of sample taken from the IE test bottles (either 1ml or 5ml) depends upon the NSSW/FW mixing ratio being evaluated in the IE test. For mixing ratios up to 70% NSSW, 1ml sample is sampled into 9ml KCl/PVS. For higher % NSSW mixing ratios 80/20, 90/10 and 95/5, 5ml is sampled into 5ml KCl/PVS – this is to ensure the $[Ba^{2+}]$ is sufficiently high (post sampling) to be assayed by ICP spectroscopy successfully.

In cases where [SI] is assayed by means of [P] by ICP spectroscopy, the 5ml sample into 5ml quenching solution sampling procedure was selected – this time to ensure the [SI] is sufficiently high enough (post sampling) to be detected by ICP spectroscopy – this is of particular importance when assaying for low [P]-containing P-tagged polymers such as PPCA.

All ICP calibration standards (both barium and SI) are prepared in the appropriate diluent solution to ensure the ICP calibration standards prepared are matrix-matched with the test-samples. In the case of 1ml sampling into 9ml KCl/PVS, the diluent solution is KCl/PVS quenching solution. In the case of 5ml sampling into 5ml KCl/PVS, the diluent solution contains appropriate concentrations of brine ions (excluding sulphate and barium) and KCl/PVS (which is present in the IE quenching solution). The concentration of the brine ions in the diluent solution depends on which NSSW/FW mixing ratio is being tested in the IE experiment (either - 80/20, 90/10 or 95/5 NSSW/FW). For example, for mixing ratio 80/20 NSSW/FW, the diluent solution contains (by volume) 50% KCl/PVS, 40% NSSW (sulphate-free) and 10% FW.

The required efficiencies for $BaSO_4$ inhibition are then calculated using the following, Equation (11):

$$\%Efficiency(t) = \frac{(M_B - M_I)x100}{M_B} = \frac{(C_O - C_B) - (C_O - C_I)x100}{(C_O - C_B)} = \frac{(C_I - C_B)x100}{(C_O - C_B)} \quad (11)$$

Where;

$M_B$ = Mass of barium (or other cations) precipitated in supersaturated blank solution (no inhibitor)

$M_I$ = Mass of barium (or other cations) precipitated in test solution.

$C_O$ = Concentration of barium (or other cations) originally in solution (i.e. t=0).

$C_I$ = Concentration of barium (or other cations) at sampling.

$C_B$ = Concentration of barium (or other cations) in the blank solution (no inhibitor) at the same conditions and sampling time as $C_I$ above.

(t) = Sampling time.

**Note:** $C_O$ is determined by adding the test NSSW and Forties FW to the KCl/PVS quenching solution in the appropriate ratio, as used for the quenched test solutions. $C_O$ samples are added to the ICP analysis of test samples at regular intervals to allow for instrumental errors to be accounted for.

***Base Case IE Experiments*** used North Sea Seawater (NSSW) and Forties Formation Water (FW) as detailed in Table A6/7.1 and Table A6/7.2. The $[Ca^{2+}]$ and $[Mg^{2+}]$ in the

produced water depends upon the mixing ratio of NSSW/FW being evaluated in the normal Base Case conditions.

| Ion | Conc. / ppm | Formula |
|---|---|---|
| $Na^+$ | 10890 | NaCl |
| $Ca^{2+}$ | 428 | $CaCl_2.6H_2O$ |
| $Mg^{2+}$ | 1368 | $MgCl_2.6H_2O$ |
| $K^+$ | 460 | KCl |
| $Ba^{2+}$ | 0 | $BaCl_2.2H_2O$ |
| $Sr^{2+}$ | 0 | $SrCl_2.6H_2O$ |
| $SO_4^{2-}$ | 2960 | $Na_2SO_4$ |
| $Cl^-$ | 19773 | – |

Table A6/7.1: North Sea Seawater (NSSW) composition – Base Case experiments

| Ion | Conc. / ppm | Formula |
|---|---|---|
| $Na^+$ | 31275 | NaCl |
| $Ca^{2+}$ | 2000 | $CaCl_2.6H_2O$ |
| $Mg^{2+}$ | 739 | $MgCl_2.6H_2O$ |
| $K^+$ | 654 | KCl |
| $Ba^{2+}$ | 269 | $BaCl_2.2H_2O$ |
| $Sr^{2+}$ | 771 | $SrCl_2.6H_2O$ |
| $SO_4^{2-}$ | 0 | $Na_2SO_4$ |
| $Cl^-$ | 55279 | – |

Table A6/7.2: Forties FW composition – Base Case experiments

***Fixed Case IE Experiments*** used NSSW containing no $Ca^{2+}$ and no $Mg^{2+}$ as given in Table A6/7.3. In all Fixed Case tests, the FW contains appropriate quantities of $Ca^{2+}$ and $Mg^{2+}$ such that the final brine mix always contains 2000ppm $Ca^{2+}$ and 739ppm $Mg^{2+}$, regardless of the initial NSSW/FW mixing ratio. Table A6/7.4 and Table A6/7.5 give the FW compositions used in the Fixed Case IE tests.

| Ion | Conc. / ppm | Formula |
|---|---|---|
| $Na^+$ | 10890 | NaCl |
| $Ca^{2+}$ | 0 | $CaCl_2.6H_2O$ |
| $Mg^{2+}$ | 0 | $MgCl_2.6H_2O$ |
| $K^+$ | 460 | KCl |
| $Ba^{2+}$ | 0 | $BaCl_2.2H_2O$ |
| $Sr^{2+}$ | 0 | $SrCl_2.6H_2O$ |
| $SO_4^{2-}$ | 2960 | $Na_2SO_4$ |
| $Cl^-$ | 15026 | – |

Table A6/7.3: North Sea Seawater (NSSW) composition - Fixed Case experiments

| Ion | Conc. / ppm | Formula |
|---|---|---|
| $Na^+$ | 31275 | NaCl |
| $Ca^{2+}$ | See Tables A.6/7-5 – A.6/7-9 | $CaCl_2.6H_2O$ |
| $Mg^{2+}$ | See Tables A.6/7-5 – A.6/7-9 | $MgCl_2.6H_2O$ |
| $K^+$ | 654 | KCl |
| $Ba^{2+}$ | 269 | $BaCl_2.2H_2O$ |
| $Sr^{2+}$ | 771 | $SrCl_2.6H_2O$ |
| $SO_4^{2-}$ | 0 | $Na_2SO_4$ |
| $Cl^-$ | See Tables A6/7.5 – A6/7.9 | – |

Table A6/7.4: Forties FW composition – Fixed Case experiments (except $Ca^{2+}$, $Mg^{2+}$ & $Cl^-$)

| Mixing Ratio NSSW/FW | FW [$Mg^{2+}$] / ppm | FW [$Ca^{2+}$] / ppm | FW [$Cl^-$] / ppm |
|---|---|---|---|
| 10/90 | 821 | 2,222 | 55,911 |
| 20/80 | 924 | 2,500 | 56,702 |
| 30/70 | 1,056 | 2,857 | 57,719 |
| 40/60 | 1,232 | 3,333 | 59,075 |
| 50/50 | 1,478 | 4,000 | 60,972 |
| 60/40 | 1,848 | 5,000 | 63,819 |
| 70/30 | 2,463 | 6,667 | 68,563 |
| 80/20 | 3,695 | 10,000 | 78,053 |
| 90/10 | 7,390 | 20,000 | 106,520 |

Table A6/7.5: Formation Water $Ca^{2+}$, $Mg^{2+}$ and $Cl^-$ content – applying to all Fixed Case IE experiments. NB: FW composition for 40/60 NSSW/FW is given for information only – this mixing ratio was not tested in any experiment.

***Varying the Mixed Molar Ratio IE Experiments*** used brines which were slightly more complex in that a variety of different FW compositions are required, each FW containing a different concentration of $Ca^{2+}$ and $Mg^{2+}$. Table A6/7.6, Table A6/7.7, Table A6/7.8 and Table A6/7.9 give the FW brine $Ca^{2+}$, $Mg^{2+}$ and $Cl^-$ for the experiments testing PPCA, MAT, SPPCA, PFC, PMPA, CTP-A, CTP-B, DETPMP and HMTPMP. In these cases, the other FW ion concentrations ($Na^+$, $K^+$, $Ba^{2+}$ and $Sr^{2+}$) are given in Table A6/7.4. The FW is always mixed with Fixed Case "blank" NSSW which contains 0ppm $Ca^{2+}$ and 0ppm $Mg^{2+}$ (see Table A6/7.3).

| **Molar Ratio $Ca^{2+}/Mg^{2+}$** | **$[Ca^{2+}]$ / ppm** | **$[Mg^{2+}]$ / ppm** | **$[Cl^-]$ / ppm $^{\Delta}$** |
|---|---|---|---|
| 1 | 2004 | 1216 | ~56675 |
| 2 | 2672 | 810 | ~56675 |
| 4 | 3206 | 486 | ~56675 |

Table A6/7.6: Formation water $Ca^{2+}$, $Mg^{2+}$ and $Cl^-$ – experiment testing DETPMP, varying Ca/Mg (Paper 6)

$^{\Delta}$ In this experiment, the total molar concentration (moles per litre) of ($[Mg^{2+}]$ + $[Ca^{2+}]$) = 0.05 (in produced water and FW), the molar chloride ion concentration and total dissolved solids concentration in the FW and final mix of brines remains almost constant therefore so does the level of supersaturation.

| **Ion ↓ Ca/Mg (FW & MIX) →** | **Molar ratios 0** | **0.05** | **0.1** | **0.15** | **0.25** | **0.35** | **0.5** | **0.75** | **1** | **1.25** | **1.5** | **1.64** | **5** | **10** | ∞ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **$Ca^{2+}$ / ppm** | 0 | 765 | 1465 | 2100 | 3220 | 4170 | 5365 | 6895 | 8045 | 8940 | 9655 | 10000 | 13410 | 14630 | 16090 |
| **$Mg^{2+}$ / ppm** | 9760 | 9295 | 8875 | 8485 | 7810 | 7230 | 6505 | 5575 | 4880 | 4340 | 3905 | 3695 | 1625 | 885 | 0 |
| **$Cl^-$ / ppm** | ~78053 | ~78053 | ~78053 | ~78053 | ~78053 | ~78053 | ~78053 | ~78053 | ~78053 | ~78053 | ~78053 | ~78053 | ~78053 | ~78053 | ~78053 |

Table A6/7.7: Formation water $Ca^{2+}$, $Mg^{2+}$ and $Cl^-$ – experiments testing PPCA, MAT and SPPCA, varying Ca/Mg (Paper 7)

| Molar Ratio $Ca^{2+}/Mg^{2+}$ | $[Ca^{2+}]$ FW / ppm | $[Mg^{2+}]$ FW / ppm | FW $[Cl^-]$ / ppm |
|---|---|---|---|
| 0 | 0 | 4880 | ~63818 (constant) |
| 0.1 | 733 | 4438 | ~63818 (constant) |
| 0.25 | 1610 | 3905 | ~63818 (constant) |
| 1 | 4023 | 2440 | ~63818 (constant) |
| 5 | 6705 | 813 | ~63818 (constant) |
| ∞ | 8045 | 0 | ~63818 (constant) |

Table A6/7.8: Formation water $Ca^{2+}$, $Mg^{2+}$ and $Cl^-$ – experiment testing CTP-A and CTP-B, varying Ca/Mg (Paper 7)

| Ion | $Ca^{2+}/Mg^{2+}$ = 0.19 expt. / ppm | $Ca^{2+}/Mg^{2+}$ = 0.57 expt. / ppm | $Ca^{2+}/Mg^{2+}$ = 1.64 expt. / ppm |
|---|---|---|---|
| $Ca^{2+}$ | 1158 | 2000 | 4500 |
| $Mg^{2+}$ | 3693 | 739 | 1665 |
| $Cl^-$ | ~62402 * | ~55279 * | ~62402 * |

Table A6/7.9: Formation water $Ca^{2+}$, $Mg^{2+}$ and $Cl^-$ – experiments testing polymers (Paper 7)

*The $[Cl^-]$ and ionic strength of the *produced water* in the 3 experiments testing PFC is *constant*. This is because in the Base Case experiment ($Ca^{2+}/Mg^{2+}$ = 0.57), the above FW is mixed with Base Case NSSW (Table A6/7.1), which contains 428ppm $Ca^{2+}$ and 1368ppm $Mg^{2+}$ ($[Cl^-]$ = 19773ppm), whereas in the experiments where $Ca^{2+}/Mg^{2+}$ = 0.19 and 1.64, the above FWs are mixed with Fixed Case NSSW (Table A6/7.3) which contains 0ppm $Ca^{2+}$ and 0ppm $Mg^{2+}$ ($[Cl^-]$ = 15026ppm).

*Where PFC is tested* with $Ca^{2+}/Mg^{2+}$ = 0.19, 0.57 and 1.64, in the $Ca^{2+}/Mg^{2+}$ = 0.57 test, Base Case brines are used (Table A6/7.1 and Table A6/7.2); this is the molar ratio $Ca^{2+}/Mg^{2+}$ in the brine mix which occurs naturally when these two brines are mixed. When additional molar ratios $Ca^{2+}/Mg^{2+}$ = 0.19 and 1.64 are tested, the total number of moles of $Ca^{2+}$ and $Mg^{2+}$ in the brine mix stayed the same as in the $Ca^{2+}/Mg^{2+}$ = 0.57 mix, but Fixed Case NSSW is used, which contained 0ppm $Ca^{2+}$ and 0ppm $Mg^{2+}$ (Table A6/7.3), and mixed with the FWs given in Table A6/7.9. The produced water total number of moles of ($Ca^{2+}$+$Mg^{2+}$), $X_m$ is fixed = 72.3millimoles/L, only the molar ratio

$Ca^{2+}/Mg^{2+}$ varies between these experiments, therefore total dissolved solids (ppm) varied but ionic strength (moles/L) remained constant. This can be illustrated by calculation (using the chloride ion concentration):

In the Base Case 60/40 NSSW/FW $Ca^{2+}/Mg^{2+}$ = 0.57 test ($X_m$ = 72.3mM/L):
$[Cl^-]$ (mix) = {(0.6*19773)+(0.4*55279)} = (11863.8+22111.6) = ~ 33975ppm

In the 60/40 NSSW/FW $Ca^{2+}/Mg^{2+}$ = 0.19 and 1.64 tests ($X_m$ = 72.3mM/L):
$[Cl^-]$ (mix) = {(0.6*15026)+(0.4*62402)} = (9015.6+24960.8) = ~ 33976ppm

Therefore, both the ionic strength and produced water $[Cl^-]$ are constant in the PFC experiments varying $Ca^{2+}/Mg^{2+}$ = 0.19, 0.57 and 1.64 (Paper 7).

***Static Compatibility Tests***

Two static compatibility experiments involving PPCA are carried out. For these experiments, sulphate-free NSSW (Fixed Case composition) is used in one case – see Table A6/7.10, and FW containing no $Ba^{2+}$ and no $Sr^{2+}$ is used in both cases (Fixed Case 80/20 NSSW/FW composition) – see Table A6/7.11.

| Ion | Conc. / ppm | Formula |
|---|---|---|
| $Na^+$ | 11598 * | NaCl |
| $Ca^{2+}$ | 0 | $CaCl_2.6H_2O$ |
| $Mg^{2+}$ | 0 | $MgCl_2.6H_2O$ |
| $K^+$ | 460 | KCl |
| $Ba^{2+}$ | 0 | $BaCl_2.2H_2O$ |
| $Sr^{2+}$ | 0 | $SrCl_2.6H_2O$ |
| $SO_4^{2-}$ | 0 | $Na_2SO_4$ |
| $Cl^-$ | 18303 * | – |

Table A6/7.10: Sulphate-free NSSW (no $Ca^{2+}$, no $Mg^{2+}$) composition – used in one of the compatibility experiments testing PPCA

*extra NaCl added to maintain ionic strength of the produced water to same level in both static compatibility experiments.

| Ion | Conc. / ppm | Formula |
|---|---|---|
| $Na^+$ | 31275 | NaCl |
| $Ca^{2+}$ | 10000 | $CaCl_2.6H_2O$ |
| $Mg^{2+}$ | 3695 | $MgCl_2.6H_2O$ |
| $K^+$ | 654 | KCl |
| $Ba^{2+}$ | 0 | $BaCl_2.2H_2O$ |
| $Sr^{2+}$ | 0 | $SrCl_2.6H_2O$ |
| $SO_4^{2-}$ | 0 | $Na_2SO_4$ |
| $Cl^-$ | 77290 | – |

Table A6/7.11: Barium and strontium free FW – used in both compatibility experiments testing PPCA

***Hyamine Assayed Test-Samples***

Refer to A.5.1 for the background of this analytical technique and the experimental procedure.

In experiments where test-samples are analysed for [SI] by means of the C18/ Hyamine technique, in addition to taking a sample for ICP analysis (sampled into a test-tube), a 25ml sample is taken from each test-bottle and added to 25ml of PVS-containing quenching solution (into a 100ml plastic bottle). A larger volume of sample is required for the C18/Hyamine analysis. Furthermore, since this procedure clearly involves removing a large volume of liquid from each test bottle – in the static IE test, separate test bottles are heated (in duplicate) for each sampling time, i.e. 2 bottles for the 0.5 hour test, 2 bottles for the 1 hour test, etc. Only 2 blank bottles require to be heated, since only one sample is taken from these 2 SI-free bottles for SI analysis (at the final sampling time).

***Pinacyanol Assayed Test-Samples***

Where there is a need to assay test-samples for sulphonated SI, a DETPMP-containing quenching solution is used rather than a PVS-containing one. The procedure is exactly the same as described in A.1, except that DETPMP replaces PVS or PPCA. In one instance where PFC (a sulphonated SI) is assayed by ICP and by the Pinacyanol Chloride Blue dye method, two sets of test-tubes were prepared for the IE sampling. One set of test-tubes contained 5ml of PVS-containing quenching solution. These samples were for the ICP analysis for [PFC] by means of [P], and so this quenching solution had to be DETPMP-free. The other set of test-tubes contained 5ml of DETPMP-containing quenching solution. These samples were for the Pinacyanol

Chloride Blue dye determination of [PFC], and so this quenching solution had to be PVS-free. Any PVS present would also react with the Pinacyanol Chloride reagent, creating false, enhanced results for [PFC].

For sulphonated scale inhibitors such as PFC, PVS, VS-Co, SPPCA, etc., analysis by the Hyamine 1622 method is very poor, since separation of the inhibitors using C18 cartridges is not possible due to the ionic nature of the sulphonic acid group. Without separation from brine electrolytes, the Hyamine 1622 method gives very poor analysis due to interferences, particularly from chloride ions. In order to assay the various polyvinyl sulphonate inhibitors and co-polymers containing vinyl sulphonate groupings, several unpublished analytical procedures were obtained from Marathon and Baker Performance Chemicals. A method very similar to that was examined in more detail and shown to be acceptable in synthetic Sea Water (McTeir, M.D.K. 1993). Due to the presence of interfering brine electrolytes, the method is inherently less accurate than the methods reported for phosphonate and PPCA inhibitors. However, due to the very short time required for this analytical technique, repeat analysis allows for the statistical accuracy to be greatly improved. It is recommended that at least three separate assays are conducted for each sample. Furthermore, this analytical technique gives a curve, which requires many points for calibration.

**Note:** The previously mentioned $NH_2$ cartridges for the successful analysis of sulphonated products in Paper 5 were not used here as the analysis developments and the research for Papers 6 and 7 were being performed simultaneously.

**Procedure**

1. Dilute a SI/DW stock solution down to make 20ml standards at concentrations: 0, 1, 2, 5, 8, 10, 15, 20 and 30ppm (active) in the appropriate matrix i.e. NSSW, FW, etc., with which to determine a calibration curve.
2. Add 1ml of the standard inhibitor solutions to 20ml of freshly prepared pinacyanol dye solution.
3. After exactly 2 minutes (after addition of 1ml test sample to 20ml dye solution, measure the absorbance of each sample at 485nm in a 2cm cell, using the UV/visible scanning spectrophotometer. Use a stop clock to measure the 2 minute time interval. 485nm is within the visible range of light. **Note:** Ensure the 2cm cell

is cleaned and rinsed thoroughly between test samples, thus ensuring no residual dye is present in the cell which could skew absorbance readings.

4. Subtract the 0ppm (blank) absorption signal from that of the standards and plot a normalised calibration curve with absorbance on the x-axis and the SI concentration on the y-axis.*
5. Perform repeats at known concentrations, e.g. 2 and 10ppm to determine the repeatability of the method using the previously constructed calibration graph. Analyse blank (0ppm) samples before and after a run of analysis (to allow for drifts).
6. Repeat the process for samples and determine the concentration of the chemical in the solution using their recorded absorbance values and the previously constructed calibration graph.

* Due to the instability of the dye solution once prepared, the calibration samples should be analysed immediately prior to analysis of repeat samples or actual test samples, using the same freshly prepared dye solution.

# Appendix B Thesis Publications

**Paper 1:** Graham, G.M., Boak, L.S. and Sorbie, K.S.: "The Influence of Formation Calcium and Magnesium on the Effectiveness of Generically Different Barium Sulphate Oilfield Scale Inhibitors", *SPE Production and Facilities*, Vol. 18, Issue No. 1, pp.28 - 44, February 2003.

**Paper 2:** Graham, A.L., Boak, L.S., Neville, A. and Sorbie, K.S.: "How Minimum Inhibitor Concentration (MIC) and Sub-MIC Concentrations Affect Bulk Precipitation and Surface Scaling Rates", *SPE Production and Operations,* Vol. 21, Issue No. 1, pp.19-25, February 2006.

**Paper 3:** Boak, L.S. and Sorbie, K.S.: "The Kinetics of Sulphate Deposition in Seeded and Unseeded Tests", *SPE Production and Operations*, Vol. 22, Issue No. 4, pp.442-450, November 2007.

**Paper 4:** Kahrwad, M., Sorbie, K.S. and Boak, L.S.: "Coupled Adsorption /Precipitation of Scale Inhibitors: Experimental Results and Modelling", *SPE Production and Operations*, Vol. 24, Issue No. 3, pp.481-491, August 2009 (Online 30th July 2009).

**Paper 5:** Boak, L.S. and Sorbie, K.S.: "New Developments in the Analysis of Scale Inhibitors", *SPE Production and Operations*, Vol. 25, Issue No. 4, pp.533-544, November 2010.

**Paper 6:** Shaw, S.S., Sorbie, K.S. and Boak, L.S.: "The Effects of Barium Sulphate Saturation Ratio, Calcium and Magnesium on the Inhibition Efficiency: I Phosphonate Scale Inhibitors", *SPE Production and Operations,* Vol. 27, Issue No. 3, pp.306-317, August 2012.

**Paper 7:** Shaw, S.S., Sorbie, K.S. and Boak, L.S.: "The Effects of Barium Sulphate Saturation Ratio, Calcium and Magnesium on the Inhibition Efficiency: II Polymeric Scale Inhibitors", *SPE Production and Operations,* Vol. 27, Issue No. 4, pp.390-403, November 2012.

## Appendix C Supporting Publications in this Thesis by L.S. Boak

1. Graham, G.M., Sorbie, K.S., Boak, L.S., Taylor, K. and Blilie, L.: “Development and Application of Accurate Detection and Assay Techniques for Oilfield Scale Inhibitors in Produced Water Samples”, SPE 28997, SPE International Symposium on Oilfield Chemistry, San Antonio, Texas, USA, 14-17 February 1995.
2. Graham, G.M., Sorbie, K.S. and Boak, L.S.: “Development and Accurate Assay Techniques for Poly Vinyl Sulphonate (PVS) and Sulphonated Co-polymer (VS-Co) Oilfield Scale Inhibitor”, 6th International Symposium of Oilfield Chemicals, Geilo, Norway, 19-22 March 1995.
3. Graham, G.M., Sorbie, K.S., Johnston, A. and Boak, L.S.: “Complete Chemical Analysis of Produced Water by Modern Inductively Coupled Plasma Spectroscopy (ICP)”, 7th International Symposium of Oilfield Chemicals, Dr Holms Hotel, Geilo, Norway, 17-20 March 1996.
4. Graham, G.M., Boak, L.S. and Sorbie, K.S.: “The Influence of Formation Calcium on the Effectiveness of Generically Different Barium Sulphate Oilfield Scale Inhibitors”, SPE 37273, SPE International Symposium on Oilfield Chemistry, Houston, Texas, 18-21 February 1997.
5. Boak, L.S., Graham, G.M. and Sorbie, K.S.: “The Influence of Divalent Cations on the Performance of $BaSO_4$ Scale Inhibitor Species”, SPE 50771, SPE International Symposium on Oilfield Chemistry, Houston, Texas, 16-19 February 1999.
6. Graham, G.M., Boak, L.S. and Hobden, C.M.: "Examination of the Effect of Generically Different Scale Inhibitor Species (PPCA and DETPMP) on the Adherence and Growth of Barium Sulphate Scale on Metal Surfaces", SPE 68298, SPE 3rd International Symposium on Oilfield Scale, Aberdeen, Scotland, 30-31 January 2001.
7. Labille, S., Neville, A., Graham, G.M. and Boak, L.S.: “An Assessment of Adhesion of Scale and Electrochemical Pre-treatment for the Prevention of Scale Deposition on Metal Surfaces”, SPE 74676, Proceedings of the 4$^{th}$ International Symposium on Oilfield Scale, Society of Petroleum Engineers, January 2001.
8. Graham, G.M., Mackay, E.J., Wattie, I. and Boak, L.S.: "Scale Inhibitor Selection Criteria for Downhole (SQUEEZE) Application in a High Volume Horizontal Wells in a Fractured Chalk Reservoir", SPE 65025, SPE International Symposium on Oilfield Chemistry, Houston, Texas, 13-16 February 2001.

9. Boak, L.S., Graham G.M., and Hobden, C.M.: "The Effect of a Polymeric and a Phosphonate Scale Inhibitor on the Adherence and Growth of $BaSO_4$ on Hastelloy C276", Paper A1450, 13th International Conference on Crystal Growth, Kyoto, Japan, July 2001.
10. Labille, S., Neville, A., Graham, G.M. and Boak, L.S.: "An Assessment of Adhesion of Scale and Electrochemical Pre-treatment for the Prevention of Scale Deposition on Metal Surfaces", Journal of Petroleum Technology, Dec 2002, pp.51-52.
11. Boak, L.S., Graham G.M., and Jeannot, M.: "Effect of Corrosion Inhibitor and Scale Inhibitor Additives on Growth of Sulphate Scales at Metal Surfaces" SPE80394, SPE 5th International Symposium on Oilfield Scale, Aberdeen, UK, 29-30 January 2003.
12. Graham, A.L., Vieille, E., Neville, A., Boak, L.S. and Sorbie, K.S.: "Inhibition of $BaSO_4$ at a Hastelloy Metal Surface and in Solution: The Consequences of Falling Beneath the Minimum Inhibitor Concentration (MIC)", SPE 87444, 6th International Symposium on Oilfield Scale, Aberdeen, UK, 26-27 May 2004.
13. Graham, A.L., Boak, L.S., Neville, A. and Sorbie. K.S.: "How Minimum Inhibitor Concentration (MIC) and Sub-MIC Concentrations Affect Bulk Precipitation and Surface Scaling Rates", SPE 93311, 2005 SPE International Symposium on Oilfield Chemistry, Houston, Texas, U.S.A., 2 – 4 February 2005.
14. Boak, L.S., Al-Mahrouqi, H., Mackay, E.J., Inches, C.E., Sorbie, K.S., Bezerra, M.C.M. and Mota, R.O.: "What Level of Sulphate Reduction is Required to Eliminate the need for Scale Inhibitor Squeezing?", SPE 95089, 7th International Symposium on Oilfield Scale, Aberdeen, UK, 11-12 May 2005.
15. Boak, L.S. and Sorbie, K.S.: "The Kinetics of Sulphate Deposition in Seeded and Unseeded Tests", SPE 100513, 2006 SPE international Oilfield Scale Symposium, Aberdeen, UK, 30 May-1 June 2006.
16. Boak, L.S., Sorbie, K.S. and Ziadi, C.: "Barite Deposition Kinetic Studies: Flow Cell Experimental Results and Modelling", 18th NIF International Oilfield Chemistry Symposium, Geilo, Norway, 25-28th March 2007.
17. Kahrward, M., Sorbie, K.S., Boak, L.S.: "Coupled Adsorption/Precipitation of Scale Inhibitors: Experimental Results and Modelling", SPE 114108, SPE 9th International Conference on Oilfield Scale, Aberdeen, UK, 28-29 May 2008.
18. Patroni Zavala, J.A., Mackay, E.J., Vazquez, O., Boak, L.S., Singleton, M. and Ross, G.: "The Cost and Value of Field, Laboratory and Simulation Data for

Validating Scale Inhibitor Treatment Models", SPE 114106, SPE 9th International Conference on Oilfield Scale, Aberdeen, UK, 28-29 May 2008.

19. Boak, L.S. and Sorbie, K.S.: "New Developments on the Analysis of Scale Inhibitors", SPE 130401, SPE International Conference on Oilfield Scale, Aberdeen, UK, 26-27 May 2010.
20. Shaw, S.S., Sorbie, K.S. and Boak, L.S.: "The Effects of Barium Sulphate Saturation Ratio, Calcium and Magnesium on the Inhibition Efficiency: I Phosphonate Scale Inhibitors", SPE 130373, SPE International Conference on Oilfield Scale, Aberdeen, UK, 26-27 May 2010.
21. Shaw, S.S., Sorbie, K.S. and Boak, L.S.: "The Effects of Barium Sulphate Saturation Ratio, Calcium and Magnesium on the Inhibition Efficiency: II Polymeric Scale Inhibitors", SPE 130374, SPE International Conference on Oilfield Scale, Aberdeen, UK, 26-27 May 2010.
22. Ibrahim, J., Sorbie, K.S. and Boak, L.S.: "Coupled Adsorption/Precipitation Equipments: 1. Static Results", SPE 155109, SPE International Conference on Oilfield Scale, Aberdeen, UK, 30-31 May 2012.
23. Ibrahim, J., Sorbie, K.S. and Boak, L.S.: "Coupled Adsorption/Precipitation Equipments: 2. Non-Equilibrium Sand Pack Treatment", SPE 155110, SPE International Conference on Oilfield Scale, Aberdeen, UK, 30-31 May 2012.